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ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL FOR THE PETROCHEMICAL INDUSTRY, VOLUME 2

ACRYLONITRILE MANUFACTURE

AIR PRODUCTS AND CHEMICALS, INCORPORATED

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

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This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by twelve distinctly different processes has been selected for this type of in-depth study. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006-a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005-a, b, c, and d).

This volume covers the manufacture of acrylonitrile. Included is a process and industry description, an engineering description of available emission control systems, the cost of these systems, and the financial impact of emission control on the industry. Also presented are suggested air episode procedures and plant inspection procedures.

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PETROCHEMICAL AIR POLLUTION STUDY

INTRODUCTION TO SERIES

This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by 12 distinctly different processes has been selected for this type of in-depth study. These processes are considered to be ones which might warrant standards as a result of their impact on air quality. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c and d).

The ten volumes of this series report on carbon black, acrylonitrile, ethylene dichloride, phthalic anhydride (two processes in a single volume), formaldehyde (two processes in two volumes), ethylene oxide (two processes in a single volume) high density polyethylene, polyvinyl chloride and vinyl chloride monomer.

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The study reported in this volume, by its nature, relied on the fullest cooperation of the companies engaged in the production of acrylonitrile. Had their inputs been withheld, or valueless, the study would not have been possible or at least not as extensive as here reported. Hence, Air Products wishes to acknowledge this cooperation by listing the contributing companies.

American Cyanamid Co.
E. I. duPont deNemours & Co.
Monsanto Company
Vistron Corporation*

*Subsidiary of Standard Oil Company (Ohio), the process licensor.

Additionally, Air Products wishes to acknowledge the cooperation of the member companies of the U. S. Petrochemical Industry and the Manufacturing Chemists Association for their participation in the public review of an early draft of this document. More specifically, the individuals who served on the EPA's Industry Advisory Committee are to be commended for their advice and guidance at these public meetings.

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SUMMARY

The acrylonitrile industry has been studied to determine the extent of air pollution resulting from the operations of the various plants and processes of the industry. The purpose of the work was to provide the Environmental Protection Agency with a portion of the basic data required in order to reach a decision on the need to promulgate air emission standards for the industry.

Although a number of chemical routes to acrylonitrile are discussed in the literature, only one, ammoxidation of propylene, is practiced to any extent, anywhere in the world. In the United States, only the Sohio fluid bed catalytic process is practiced. Therefore, this report is devoted to the study of the Sohio version of the ammoxidation of propylene, using air as the oxidant, for the production of acrylonitrile.

In general terms, the air emissions from the process fall into the categories of hydrocarbons (paraffins, olefins and nitriles), carbon monoxide, and oxides of nitrogen (primarily from waste and by-product incineration). Some traces of particulate matter (catalyst fines) and ammonia are also emitted, but not to a significant extent. The total amounts of all of these materials emitted, and the ease of removing them from the effluent gas streams are both somewhat a function of the catalyst used. The more recent catalyst developments tend to lead in the favorable direction with respect to both emissions and their control. The current (1974) generation of catalyst which contains bismuth and molybdenum is gradually replacing the older uranium (depleted) catalyst. The report has taken the effects of this changeover into consideration in arriving at emission factors ranging between 0.35 and 0.25 lbs./lb. of acrylonitrile produced. This amounted to about 400 million lbs. per year of total atmospheric emissions in 1973 which will be reduced to about 260 million lbs. per year as soon as the changeover to new catalyst is fully effected. Of those totals, slightly more than half is carbon monoxide, about one-fifth propylene and about four percent nitriles (acrylonitrile, acetonitrile and hydrogen cyanide). Assuming no further catalyst developments take place and all new plants also use the current generation catalyst, production growth can be expected to increase total emissions to nearly 900 million pounds/year by 1985, if all future plants are built as is currently typical, and if by-product incineration is practiced at the same proportionate level as has been estimated for today's operations, thus contributing an approximate three percent or 25 million pounds per year of nitrogen oxides to the total.

The chief source of air emissions from the process is the main vent from the absorber. All plants employ a mist eliminator on this stream to minimize the carryover of water (the absorbing medium) with the venting stream. However, none of the current plant operators employ any additional air pollution control devices on this stream. Hence, the study addressed itself to the task of finding a "feasible" though not "demonstrated" emission control device for these effluents. It was concluded that some form of incineration could be practiced on this stream, and that the use of a thermal incinerator equipped with feed/effluent heat exchange and supplemental fuel firing was the best technique for achieving reductions in these emissions. It was further concluded that steam generation by means of a waste heat boiler following the incinerator is a feasible means of reducing the cost of emission control, provided that the steam can be utilized. Additionally, steam generation from waste heat reduces the impact of the supplemental fuel consumption on the overall fuel supply problems of the U.S. and the world.

SUMMARY (continued)

Potentially, the second largest emission source from the process is the disposal of large amounts of acetonitrile (0.1 lbs./lb. of acrylonitrile), hydrogen cyanide (0.17 lbs./lb. of acrylonitrile) and ammonium sulfate (0.04 lbs./lb. of acrylonitrile), none of which are marketable in the quantities and/or dilutions produced. Current practice is to incinerate all unwanted HCN and to either incinerate the excess acetonitrile and ammonium sulfate (the latter under emergency conditions, only) or dispose of them as dilute water solutions in a deep well. If future ground water pollution control regulations prevent the continued use of deep well disposal techniques, significant air pollution as oxides of sulfur, could result from the incineration of ammonium sulfate. Additionally, heat requirements to incinerate these dilute water streams would be substantial. This study has concluded that waste heat from absorber vent gas incineration is sufficient to concentrate the waste acetonitrile to a point where it can be incinerated without supplemental fuel. Furthermore, it appears feasible to use the effluent from this incinerator in a spray drier to concentrate and recover the ammonium sulfate. Obviously, the incineration of these nitrile containing streams will result in the generation of some quantity of nitrogen oxides. Determination of the amounts generated and the best designs for minimizing these amounts must, by necessity, be the goal of future studies.

Minor vent streams result from product fractionation and the various storage systems. Nearly all of these streams are currently flared or burned in some other convenient manner.

Total air emissions from the acrylonitrile industry can be expected to be reduced to about 40 million lbs./year in 1985 (about 0.01 lbs./lb. of acrylonitrile) if absorber vent gas incinerators are included in all future and existing plants. However, it has been estimated that this will result in a 50 percent increase in the emission factor for nitrogen oxides (from 0.0067 to 0.0098 lbs./lb. of acrylonitrile) accounting for nearly 95 percent of the total 1985 estimated emissions from the "best controlled" version of the process. Obviously, if the proportion of by-products incinerated changes, then the nitrogen oxide emissions will also be different from this estimate.

The capital investment (1973 dollars) required for the installation of a thermal incinerator on the absorber vent of a "model" 200 MM lbs./year acrylonitrile plant has been estimated to be about $350,000. An additional $410,000 will be required to add a waste heat boiler to the system and if a highly reliable system is required, it might be deemed advisable to provide multiples of one or both of these units. The annual operating cost of a single thermal incinerator has been estimated (1973 prices) to be nearly $136,000 and a $20,000 reduction can be effected through the addition of a waste heat boiler.

The incinerator for by-product disposal from the model plant will require between $200,000 and $400,000 capital investment depending upon the capacity assigned to it and will cost between $50,000 and $70,000 per year to operate, without provision for concentration of acetonitrile and recovery of ammonium sulfate (or scrubbing of sulfur oxides if the salt solution is incinerated).

These are not significant costs to the industry, resulting in a reduction of about 3 percent in net profit after taxes and a reduction in return on total investment from 8.5 percent to about 8 percent. This is due partly to

SUMMARY (continued)

the fact that a by-product incinerator is typically part of all current plants. These profit and ROI reductions apply to both new plants and existing plants with retrofit incinerators.

The capital expenditure (1973 dollars) required for the industry to effect the reduction in emissions cited above will be about $2,000,000 for all existing plants with an additional $10,000,000 required for all future plants. This assumes a single incinerator installed on each absorber vent gas stream and a single waste heat boiler on all future plant incinerators.

The report cites three concepts for research that could lead to reduced emissions from the acrylonitrile production process. Two of these could best be undertaken by the process licensor and/or operators of the process. These are (1) the use of oxygen rather than air feed to the reactor, with recycle of off gases and (2) the utilization of by-product HCN and acetonitrile for additional acrylonitrile production. The third area for research does not require any acrylonitrile production knowledge or experience and could find general application in any process for the production of organic nitrogen products. It is the development of an efficient thermal incineration system that minimizes nitrogen oxide formation.

I. Introduction

Although a variety of chemical routes to acrylonitrile exist, present practice concentrates exclusively on the ammoxidation of propylene. Several processes based on this reaction are used throughout the world, however, only the Sohio fluid bed catalytic process, using air as the oxidant, is employed in the United States.

Atmospheric emissions from this ammoxidation process consist of water vapor, carbon dioxide, carbon monoxide, C_3 hydrocarbons, NO_x, nitriles and nitrogen. The amount of nitrogen compounds emitted is somewhat influenced by the amount of by-product hydrogen cyanide (HCN) and acetonitrile that can be marketed.

A process description, industry survey of emission sources, effluent characteristics, control practices and equipment in addition to plant economics for the ammoxidation of propylene process are presented in the following sections.

II. Process Description and Typical Material Balance

The basic chemical equation for this process is as follows:

$$2\ CH_2{=}CH{-}CH_3 + 2\ NH_3 + 3\ O_2 \longrightarrow 2\ CH_2{=}CH{-}CN + 6\ H_2O$$

Approximately stoichiometric proportions of air, ammonia and propylene are introduced into a fluid bed reactor at 5-30 psig and 750-950° F. Once-through flow is used since conversion of propylene is virtually complete. The reaction is exothermic so heat removal must be provided. The reaction heat is normally used to generate steam by heat exchange and the effluent is then sent to a water quench tower where acid is added for neutralization of unconverted ammonia. The stream is then charged to a water absorber-stripper system in order to reject inert gases and recover reaction products. This operation yields a miaxure of acetonitrile, acrylonitrile and HCN which is usually first fractionated to remove HCN. Next, acetonitrile is separated from the HCN tower bottoms by extractive distillation (with water as the extraction solvent). The final two steps involve drying of the acrylonitrile stream (obtained overhead from the acetonitrile separation column) and a final distillation to remove heavy ends. The acrylonitrile product thus obtained is 99+% pure.

Figure AN-1 shows a flow diagram for a typical plant and indicates the various vent streams from the unit.

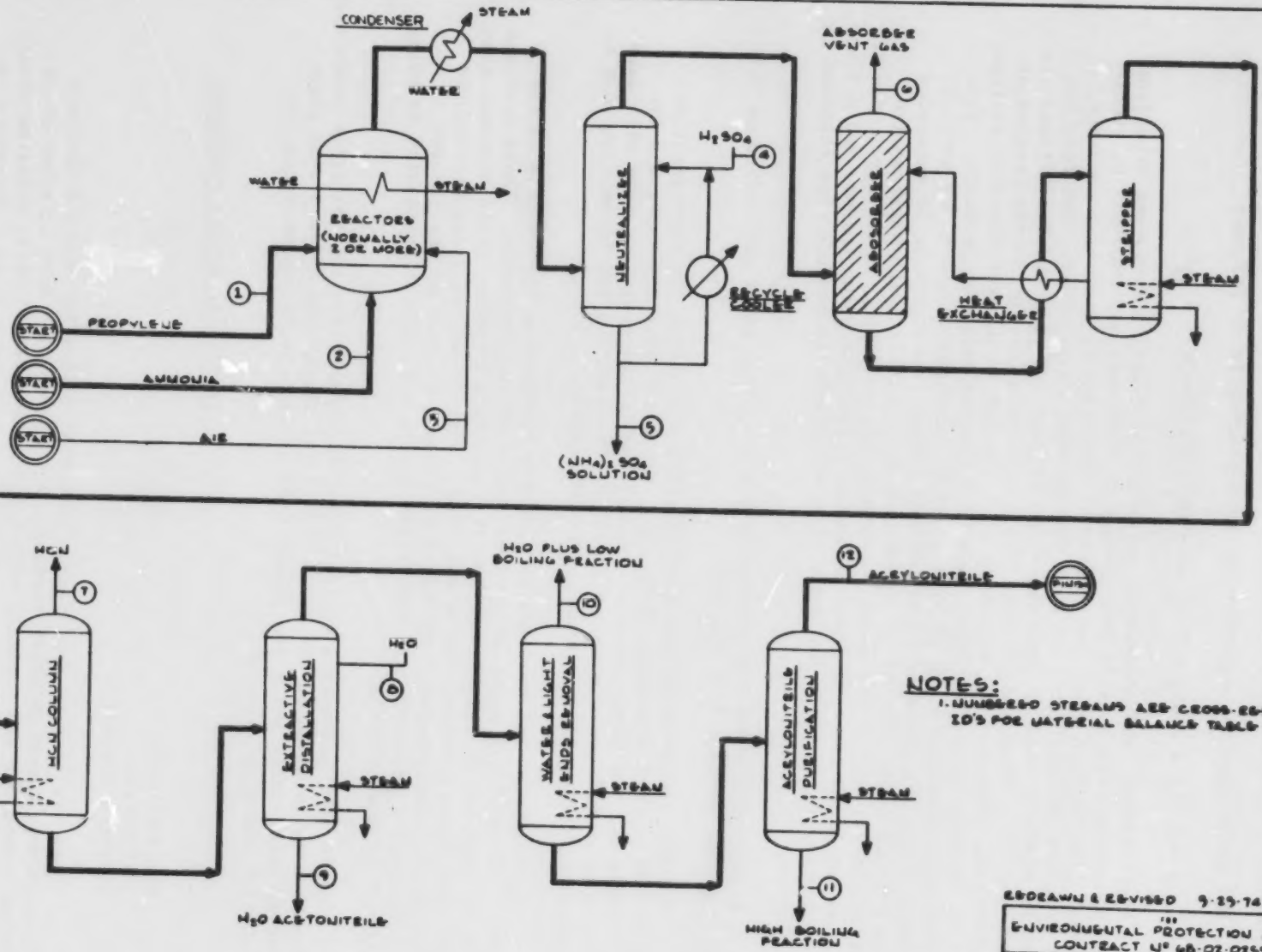
Primary raw material for acrylonitrile production are refrigeration grade ammonia and propylene ($\geq$90% $C_3^=$). No alternative raw materials are available for the Sohio process. Impurities in the propylene feed with less than four carbon atmos are unaffected by the reaction, but those with four or more participate and, therefore, are undesirable.

Acetonitrile and hydrogen cyanide are produced as by-products in the amount of about 0.1 pound of each per pound of acrylonitrile. These products can be produced at salable purity (99+% purity); however, it is doubtful that the quantities produced can be marketed. Part or all of these by-products are usually incinerated. It should be noted that four of the present acrylonitrile producers are not listed by the U.S. Tariff Commission as being sellers of acetonitrile.

Table AN-1 presents a typical material balance for acrylonitrile production. The balance is based on the following yields which were derived from plant survey data, taken while the plants were using Sohio's depleted uranium catalyst (Catalyst 21):

	LB./LB. Propylene Converted
Acrylonitrile	0.84
Acetonitrile	0.09
Hydrogen Cyanide	0.145

These yields also approximate published values for Sohio's obsolete bismuth/molybdenum catalyst (Catalyst A). Currently, even Catalyst 21 is being phased out and replaced with Sohio's Catalyst 41 which achieves about the same yields but provides better utilization of ammonia. Therefore, a smaller amount of acid is required for downstream neutralization. Typical ammonia feed rates for various catalysts currently in service vary between 0.39 and 0.56 pounds per pound of propylene feed. Catalyst 41 also requires less excess oxygen and, therefore, less nitrogen in the vent gas.



AN-3

NOTES:

1. NUMBERED STREAMS ARE CROSS-REFERENCE ID'S FOR MATERIAL BALANCE TABLE AN-1

SCALE	NONE	DATE
DRAWN BY	B.H.	7-18-72
CHECKED BY	R.C.B	7-23-74
CATALYTIC APPROVAL		
CLIENT APPROVAL		

REDRAWN & REVISED 9-29-74

FOR ENVIRONMENTAL PROTECTION AGENCY CONTRACT No 68-02-0255

PREPARED BY CATALYTIC, INC. ENGINEERING DEPARTMENT IN CHARLOTTE, N.C.

FIGURE AN-1

SIMPLIFIED FLOW DIAGRAM FOR ACRYLONITRILE PRODUCTION

CONTRACT 42030 | DWG. NO. R-213 | REV. NO. Δ

APP. NO. 909

TABLE AN-1
TYPICAL MATERIAL BALANCE FOR
SOHIO ACRYLONITRILE UNIT
PRODUCING 200 MM LBS./YR. ACRYLONITRILE (a)

Component	1 Propylene Feed	2 Ammonia Feed	3 Air to Reactor	4 Sulfuric Acid to Neutralizer	5 Ammonium Sulfate Solution	6 Absorber Vent Gas
Particulates (b)						TR
Carbon Dioxide						11,171
Carbon Monoxide						4,466
Ammonia		12,953				
Propylene	31,454					1,956
Propane	3,495					3,495
Hydrogen Cyanide						30
Acrylonitrile						248
Acetonitrile						95
Nitrogen		65	207,204			207,056
Oxygen			63,002			15,664
Sulfuric Acid				3,708		
Ammonium Sulfate					4,994	
Oxygenated Hydrocarbons						
Organic Polymers						
Water			2,945		29,541	14 191
Total Lbs./Hr.	34,949	13,018	273,151	3,708	34,535	258,379

Component	7 Hydrocyanic Acid	8 Make-up Water to Product Dist.	9 Dilute Acetonitrile	10 Light Ends	11 Heavy Ends	12 Acrylonitrile Product
Particulates (b)						
Carbon Dioxide				47		
Carbon Monoxide						
Ammonia						
Propylene				2		
Propane						
Hydrogen Cyanide	4,202			44		
Acrylonitrile	22			50		74,510
Acetonitrile			2,424 (c)		50	75
Nitrogen				213		
Oxygen				63		
Sulfuric Acid	2					
Ammonium Sulfate						
Oxygenated Hydrocarbons				4		
Organic Polymers					150	74
Water	13	50,306	48,006	2,300 (c)		74
Total Lbs./Hr.	4,239	50,306	50,430	2,723	200	74,633

(a) Based on using Sohio's Catalyst 21 which is currently being phased out of all domestic acrylonitrile plants, when operating with Catalyst 41, air rate is reduced by 20 percent and ammonia feed is about eight percent lower. Improved utilization of ammonia reduces sulfuric acid requirement and ammonium sulfate production to 25 percent of values shown.

(b) Catalyst particles.

(c) Can be rejected as a separate stream.

Table AN-1 material balance is for an average size plant (200 MM lbs./yr. acrylonitrile), utilizing Catalyst 21. However, since yields are about the same with Catalyst 41, this balance will be used to predict the economics of future plants (in the Model Plant Economic Studies), except that nitrogen in the vent gas, and ammonia and sulfuric acid requirements will be appropriately reduced. Table AN-1A presents the same material balance with quantities expressed as tons per ton of acrylonitrile.

At present, only one producer of acrylonitrile has completely switched over to Catalyst 41. All other producers are operating with some portion of Catalyst 21. Catalyst 41 is an improved version of the old bismuth/molybdenum catalyst.

Table AN-2 presents an estimated heat balance around the reactor system.

TABLE AN-1A
TYPICAL MATERIAL BALANCE FOR
SOHIO ACRYLONITRILE UNIT (a)

Component	1 Propylene Feed	2 Ammonia Feed	3 Air to Reactor	4 Sulfuric Acid to Neutralizer	5 Ammonium Sulfate Solution	6 Absorber Vent Gas
Particulate (b)						TR
Carbon Dioxide						0.4558
Carbon Monoxide						0.1822
Ammonia		0.5285				
Propylene	1.2833					0.0798
Propane	0.1426					0.1426
Hydrogen Cyanide						0.0012
Acrylonitrile						0.0101
Acetonitrile						0.0039
Nitrogen		0.0027	8.4539			8.4478
Oxygen			2.5705			0.6391
Sulfuric Acid				0.1513		
Ammonium Sulfate					0.2038	
Oxygenated Hydrocarbons						
Organic Polymers						
Water			0.1202		1.2053	0.5790
Total, Tons/Ton AN	1.4259	0.5312	11.1446	0.1513	1.4091	10.5415

Component	7 Hydrocyanic Acid	8 Make-up Water to Product Dist.	9 Dilute Acetonitrile	10 Light Ends	11 Heavy Ends	12 Acrylonitrile Product
Particulate (b)						
Carbon Dioxide				0.0020		
Carbon Monoxide						
Ammonia						
Propylene				0.0001		
Propane						
Hydrogen Cyanide	0.1714			0.0018		
Acrylonitrile	0.0009			0.0020		1.0000
Acetonitrile			0.0989 (c)		0.0020	0.0031
Nitrogen				0.0087		
Oxygen				0.0026		
Sulfuric Acid	0.0001					
Ammonium Sulfate						
Oxygenated Hydrocarbons				0.0002		0.0010
Organic Polymers					0.0061	0.0010
Water	0.0005	2.0525	1.9587	0.0938 (c)		
Total Tons/Ton AN	0.1729	2.0525	2.0576	0.1112	0.0081	1.0051

(a) Based on using Sohio's Catalyst 21 which is currently being phased out of all domestic acrylonitrile plants. When operating with Catalyst 41, air rate is reduced by 20 percent and ammonia feed is about eight percent lower. Improved utilization of ammonia reduces sulfuric acid requirement and ammonium sulfate production to 25 percent of values shown.

(b) Catalyst Particles

(c) Can be rejected as a separate stream.

TABLE AN-2
ACRYLONITRILE REACTOR SYSTEM
HEAT BALANCE (a)

Heat Out

Steam generation					
Cooling coils inside reactor		6,733	BTU/Lb.	of	acrylonitrile
Effluent heat recovery boiler		2,158	"	"	"
Reactor heat losses		45	"	"	"
Quench (450° ⟶ 110° F)		4,091	"	"	"
Incremental effluent heat content	(b)	- 1,000	"	"	"
	Total	12,027	"	"	"

Heat In

Exothermal heat or reaction				
Acrylonitrile formation	9,432	BTU/Lb.	of	acrylonitrile
Effluent neutralization	1,375	"	"	"
Feed vaporization and preheat	1,220	"	"	"
Total	12,027			

NOTES:

(a) Basis

1) Table AN-1A material balance (Catalyst 21).

2) Feed preheated to 300° F.

3) Reactor outlet temperature 950° F (max.).

(b) Difference in heat content of effluent @ 110° F and feed @ 80° F (liquid) plus air @ 100° F.

III. Manufacturing Plants and Emissions

Table AN-3 presents a list of U.S. plants producing acrylonitrile. Approximately half of the total production capacity is located in Texas (two producers), with the remaining acrylonitrile production in Louisiana, Ohio and Tennessee. These plants are built within five to 15 miles of towns and cities with population ranging between 10,000 and 625,000.

Table AN-3A shows individual plant capacity figures and atmospheric emission data for the various acrylonitrile plants surveyed in this study while using Catalyst 21. All of the plants included in this tabulation are about the same size (175-250 million pounds per year acrylonitrile) and represent about 85 percent of the total U.S. installed plant capacity. Emissions from these plants are as follows:

A. Continuous Air Emissions

1. Main Process Vent Gas

This stream, which vents from the absorber, consists of the gross reactor effluent after neutralization and recovery of nitriles and HCN. The process vent gas emissions presented in Table AN-3A are average values using Catalyst 21. Actual vent gas composition varies somewhat depending on type of catalyst and reactor operating conditions. Table AN-4 shows a typical breakdown of components in this stream which represents the primary air emission in the Sohio process. Vent gas composition data is shown for both catalysts currently being employed.

When absorber column overhead temperature increases, acrylonitrile emissions increase markedly (0.008 to 0.02 tons/ton acrylonitrile). One manufacturer reports this occurs about once a year with the increased acrylonitrile emissions lasting no longer than one day.

Under normal operating conditions, the quantity of absorber vent hydrocarbon emissions (excluding propane and propylene) are primarily influenced by the amount of air charged to the reactors. Since fluidized bed reactors are employed, it is necessary to maintain reactor mass flow velocity within a certain range in order to insure proper bed expansion. Therefore, air rates to individual reactors are usually held fairly constant. Plants normally have two to five reactors. At reduced plant capacity, individual reactors can be removed from service, and total absorber vent gas emissions will be reduced. Plants with only two reactors do not have as much flexibility.

In all plants, propane, propylene and carbon monoxide emissions from the absorber are directly related to acrylonitrile productivity. Since propane is not converted in the reactor, virtually all propane contained in the fresh feed will be present in the absorber vent gas.

The absorber off-gas, as is true with the other vent streams, is essentially odorless under normal operation. However, one manufacturer reports a slight odor of HCN from the absorber vent during reactor start-up. None of the plant surveys reported any particulates in this vent stream.

TABLE AN-3
SUMMARY OF U. S. ACRYLONITRILE PLANTS

Company	Location	Published Capacity, MM Lbs./Yr.
American Cyanamid Co.	South Kenner, La.	175
E. I. duPont deNemours & Co.	Beaumont, Texas	200
	Memphis, Tenn.	180
Monsanto Co.	Alvin, Texas	370
Vistron Corp.	Lima, Ohio	240
		1,165

TABLE AN-3A
SURVEY OF U. S. ACRYLONITRILE PLANTS AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number	51-1				
Date on-stream	1965				
Capacity, Tons of Acrylonitrile/Yr.	100,000 (f)				
Average Production, Tons/Yr.	100,000				
Range in Production, % of Max.	No Seasonal Variation				
Operating Range, % of Max. Prod.	50-100				
By-products (Net)					
HCN, Tons/Yr.	20,000 (g)				
Oils & Polymers, Tons/Yr.	4,000				
Emissions to Atmosphere	4,000				
Stream	Absorber Vent	Absorber Vent (During Start-up)	Product Fractionator Vent	Incinerator Flue Gas	Flare
Flow, (a) Lbs./Hr.	285,000	62,500 (o)	110	110,000 (t)	≤1,300
Flow Characteristic	Continuous	Intermittent	Continuous	Continuous	Variable
if Intermittent - Hrs./Yr. of Flow		8			
Composition, Tons/Ton Acrylonitrile					
Particulate		TR		TR	
Carbon Dioxide	0.294	0.050		X	X
Carbon Monoxide	0.180	0.032			
Ammonia		0.032		0.0003	
Methane					
Ethane & Ethylene					
Propylene	0.047	0.008			
Propane	0.124	0.030 (n)			
Hydrocyanic Acid	0.002 (b)	0.004		0.00002	
Acrylonitrile (AN)	0.029	0.225	0.0004 (b)		
Acetonitrile (ACN)	0.006 (b)	0.008	0.0003 (b)		
Oxygenated Hydrocarbons					
Nitrogen	9.726	1.676	0.004 (c)	X	X
Oxygen	0.865	0.245			X
Sulfur Oxides				0.0073	
Nitrogen Oxides				X	X
Water	0.605	0.305		Sample Line	None
Sample Tap Location	Accessible Sample Line from Reactor Effluent	Ducts	Elevated & Difficult to Reach	to Ground Level	
Date or Freq. of Sampling	Continuous For AN others twice a week	Cont. Monitor of O_2	None	Twice a Month	
Type of Analysis		Calc'd	Calc'd		Calc'd
Particulate	None			None	
HC, CO, CO_2 & Inerts	(d)			(e)	
NO_x	None			(e)	
Odor	Essentially Odorless	Slight Odor	Unknown	None	None
Color	Appearance of steam, No Residual Plume			Smokeless	Smokeless
Vent Stacks					
Number	1		1	1	1
Height	200'0"		58'0"	135'0"	275'0"
Diameter	2'6"		2"	6'0"	1'8"
SCFM per stack (a)	120	450	100	1600	≥1500
	64,600	14,300	25	24,000	≤265
Emission Control Device					
Demister	X				
Condenser			X		
Others	Flare (Distillation Lt. Ends)		Incinerator (By-product HCN & ACN)		
Total Emissions					
Hydrocarbons		0.209			
Particulates		TR			
NO_x		0.007			
SO_x					
CO		0.180			

TABLE AN-3A
SURVEY OF U. S. ACRYLONITRILE PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number	51-2			
Date on-stream	1965			
Capacity, Tons of Acrylonitrile/Yr.	125,000			
Average Production, Tons/Yr.	100,000			
Range in Production, % of Max.	No Seasonal Variation			
Operating Range, % of Max. Prod.				
By-products (Net)				
HCN, Tons/Yr.	7,000			
Acetonitrile, Tons/Yr.	3,200			
Oils & Polymers, Tons/Yr				
Emissions to Atmosphere				
Stream	Absorber Vent	Absorber Vent (During Start-up)	Incinerator Flue Gas (g)	Flare
Flow, (a) Lbs./Hr.	200,000	140,000 (o)	46,700	2,650
Flow Characteristic	Continuous	Intermittent	Continuous	Intermittent
if Intermittent - Hrs./Yr. of Flow		6-8		
Composition, Tons/Ton Acrylonitrile				
Particulate				
Carbon Dioxide	0.508	0.080	0.282	0 014
Carbon Monoxide	0.178	0.040		
Ammonia				
Methane				
Ethane & Ethylene				
Propylene	0.052	0.026		
Propane	0.144	0.027		
Hydrocyanic Acid	0.0005	0.034	< 0.000001	
Acrylonitrile (AN)	0.0004	0.608		
Acetonitrile (ACN)	0.008	0.017		
Oxygenated Hydrocarbons				
Nitrogen	7.222	5.185	1.251	0.078
Oxygen	0.303	0.218	0.174	0.002
Sulfur Oxides			0.00001	TR
Nitrogen Oxides			0.160	0 011
Water			Used 130' crane	None
Sample Tap Location	Absorber Vent			
Date or Freq. of Sampling	Nitrogen Comp'd. once a week, others in 1971		March, 1971	
Type of Analysis				Calc'd
Particulate	None		None	
HC, CO, CO_2 & Inerts	CLC (f)		CLC (f) (h)	
NO_x	Silver Nitrate Titration (f)		Silver Nitrate Titration (f)	
Odor	None		None	None
Color				
Vent Stacks				
Number	1		1	1
Height	200'0"		100'0"	200'0"
Diameter	2'6"		12'0"	2'0"
Exit Gas Temp., °F	110		1,600	1,000
SCFM per stack (e)	50,000	30,000	10,350	>600
Emission Control Device				
Demister				
Condenser				
Others	Flare (Distillation Lt. Ends (p)), 2 Incinerators (by-product HCN & ACN)			
Total Emissions				
Hydrocarbons	0.206			
Particulates				
NO_x	0.00001			
SO_x				
CO	0.178			

TABLE AN-3A
SURVEY OF U. S. ACRYLONITRILE PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number	51-3			
Date on-stream	1965			
Capacity, Tons of Acrylonitrile/Yr.	87,500			
Average Production, Tons/Yr.				
Range in Production, % of Max.	No Seasonal Variation			
Operating Range, % of Max. Prod.				
By-products (Net)				
HCN, Tons/Yr.	16,000			
Acetonitrile, Tons/Yr.				
Oils & Polymers, Tons/Yr.				
Emissions to Atmosphere				
Stream	Absorber Vent	Absorber Vent (During Start-up)	Flare	Incinerator Flue Gas
Flow, (a) Lbs./Hr.	225,000	N. A. (q)	4,100	400,000 (Max.) (j)
Flow Characteristic	Continuous	Intermittent	Continuous	Intermittent
if Intermittent - Hrs./Yr. of Flow		15		
Composition, Tons/Ton Acrylonitrile				
Particulate				
Carbon Dioxide	0.450		X	X
Carbon Monoxide	0.187			
Ammonia		0.264		
Methane	0.001			
Ethane & Ethylene	0.008			
Propylene	0.050	0.216		
Propane	0.035	0.008		
Hydrocyanic Acid				
Acrylonitrile (AN)	0.006			
Acetonitrile (ACN)				
Oxygenated Hydrocarbons				
Nitrogen	9.133		X	X
Oxygen	0.856		X	X
Sulfur Oxides				0.026
Nitrogen Oxides				
Water	0.383		X	X
Sample Tap Location	Absorber Vent Sample Line to Ground Level		None	None
Date or Freq. of Sampling	AN once every three months, other H.C. much less frequent		Not Sampled	Not Samples
Type of Analysis			None	None
Particulate	None			
HC, CO, CO_2, & Inerts	G.C.			
NO_x	None			
Odor	No problem		No problem	No problem
Color				
Vent Stacks				
Number	1		1	1
Height	200'0"		200'0"	104'0"
Diameter	2'6"		2'6"	9'0"
Exit Gas Temp., °F	105		Flame	1600
SCFM per stack (a)	50,000		< 1200 (k)	88,000 (Max.) (j)
Emission Control Device				
Demister				
Condenser				
Others	Flare (Distillation Lt. Ends), 2 Incinerator (By-products (j))			
Total Emissions				
Hydrocarbons	0.101			
Particulates				
NO_x	0.026			
SO_x	0.187			
CO				

TABLE AN-3A
SURVEY OF U. S. ACRYLONITRILE PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number	51-4				
Date on-stream	1970				
Capacity, Tons of Acrylonitrile/Yr.	110,000				
Average Production, Tons/Yr.	110,000				
Range in Production, % of Max.	Virtually No Seasonal Variation				
Operating Range, % of Max. Prod.					
By-products (Net)					
HCN, Tons/Yr.	20,000				
Acetonitrile, Tons/Yr.					
Oils & Polymers, Tons/Yr.					
Emissions to Atmosphere					
Stream	Absorber Vent	Absorber Vent (During Start-up)	Incinerator Flue Gas	Product Recovery Flare Vent	HCN Storage Flare Vent
Flow, (a) Lbs./Hr.	300,000	N. A.	98,000	2,500	750
Flow Characteristic	Continuous	Intermittent	Variable (1)	Continuous	Continuous
if Intermittent - Hrs./Yr. of Flow		2			
Composition, Tons/Ton Acrylonitrile					
Particulate		0.001			
Carbon Dioxide	0.350		0.317	0.018	0.004
Carbon Monoxide	0.167				
Ammonia					
Methane					
Ethane & Ethylene	0.001				
Propylene	0.050				
Propane	0.035				
Hydrocyanic Acid	0.006				
Acrylonitrile (AN)	0.009				
Acetonitrile (ACN)	0.003				
Oxygenated Hydrocarbons	0.0004 (m)				
Nitrogen	8.774		2.290	0.067	0.020
Oxygen	0.763				
Sulfur Oxides					
Nitrogen Oxides			0.0004 (r)	0.00001 (r)	0.00001 (r)
Water	0.787		0.709	0.005	0.002
Sample Tap Location	Absorber Vent Sample Line to Ground Level		Sample Tap Avail.	None	None
Date or Freq. of Sampling	Once a Week		Never Sampled	Never Sampled	Never Sampled
Type of Analysis			None	None	None
Particulate	None				
HC, CO, CO_2 and Inerts	GLC				
NO_x	NH_3 + HCN by Titration				
Odor	No problem		No problem	No problem	No problem
Color					
Vent Stacks					
Number	1		1	1	1
Height	224'0"		100'0"	150'0"	100'0"
Diameter	3'0"		7'6"	1'4"	6"
Exit Gas Temp., °F	113		1600		
SCFM per stack (a)	69,000		23,000 (1)	540	170
Emission Control Device					
Demister					
Condenser					
Others	Incinerator (Distillation Lt. Ends (1)), 2 Flares				
Total Emissions					
Hydrocarbons	0.102				
Particulates					
NO_x	0.0004				
SO_x					
CO	0.167				

Table AN-3A Footnotes Sheet 5 of 6

(a) Wet gas flow rate based on acrylonitrile average production rate if available, otherwise based on design capacity.

(b) Assumed composition of "miscellaneous" component.

(c) Air.

(d) Only acrylonitrile (AN) in absorber vent gas is measured directly (by gas chromatograph). Flow and composition are calculated values based on measured flows of air, propylene and ammonia into the process and on analysis of the reactor effluent. This analysis is by a combination of wet chemistry, physical separation and chromatographic techniques.

(e) Analyzed for NO_x per method 7 - Determinations of Nitrogen Oxide from Stationary Sources, Federal Register, vol. 36, No. 247, December 23, 1971. HCN and NH_3 by Draeger tubes.

(f) Gas stream is scrubbed. Scrubber solution is analysed for HCN (silver nitrate titration) AN and ACN (by gas-liquid chromatography). Scrubbed gas is analysed for other components by chromatograph (N_2 by difference).

(g) Flow rate and composition based on burning approximately 40% of by-product HCN. Incinerator designed to burn all by-products and 190 gpm of waste water. Presently all waste water (300 gpm) plus a major portion of the by-product ACN are sent to deep well disposal.

(h) Shell procedure for sulfur oxides.

(i) Company also has a 92,500 TPY plant at some location. Approximate emissions for this unit are a direct proration of values shown for the slightly larger plant.

(j) No normal flow. Incinerator only used during emergency periods when waste wash water streams containing $(NH_4)_2SO_4$ and by-product ACN are diverted from deep well disposal (once a year) and HCN can not be sent to storage (almost no chance of this occurring).

(k) Maximum flow of 58,000 SCFM during emergency. This includes combustion of feed propylene (0.331 tons/ton AN) when source of heat for propylene vaporization is lost (occurs about once every two years for two hours). Also during scheduled shut-down vaporizers are vented to flare. This vent is about 25% of emergency flow.

(l) Represents normal flow from burning some by-product nitrogen compounds rejected in product recovery section including 50 tons/month HCN. Occasionally during process upsets total by-product HCN is sent to this incineration. When this occurs flow is increased to 95,000 SCFM. On an average 100 tons/month of HCN is burned in this incinerator.

(m) Composition is approximately 49 wt. % acetaldehyde, 32% acetone and 19% acrolein.

(n) Includes 0.005 tons/ton of miscellaneous compounds not identified.

Table AN-3A Footnotes (Continued) Sheet 6 of 6

(o) This condition represents the operation during start-up of one reactor. While flow condition and composition change during the start-up, these data represent average values. Start-up time normally requires a maximum of one hour. Data shown is for start-up of one reactor of a two reactor plant. If other reactor is on-stream total vent will contain indicated flow plus 50% of normal absorber vent shown in preceding column. On an average, eight reactor start-ups per year are expected.

(p) In addition, HCN is diverted from incinerators to flare about once a year. Propylene storage tanks relieve to flare on infrequent basis.

(q) Same as comment (o) except this plant has five reactors. If other reactors are on-stream, total vent will contain indicated flow plus 80% of normal absorber vent shown in preceding column.

(r) Calculated value based on U. S. Dept. of HEW factors for calculating emissions from burning natural gas.

(s) In the near future all by-product HCN will be burned.

(t) Flow based on burning all by-product HCN and ACN.

It should be noted that flow rates and compositions shown for intermittent streams represent emissions during flowing condition and not yearly averaged values. The total plant emission figures shown are averaged emissions for extended periods of operation.

TABLE AN-4
TYPICAL VENT GAS COMPOSITION
FOR
200 MM LB./YR. ACRYLONITRILE PRODUCTION

Operation	Normal Composition (a) Mol. %		Catalyst 21			Catalyst 41 (b)	
	Range-Catalyst 21	Catalyst 41 (b)	Average Flow Rate MPH	Average Flow Rate Lbs./Hr.	Start-up Flow Rate Lbs./Hr. (c)	Average Flow Rate MPH	Average Flow Rate Lbs./Hr.
Component							
Particulate				TR	25		TR
Carbon Dioxide	1.5 - 3.7	2.6	253.9	11,171	1,593	189.6	8,342
Carbon Monoxide	1.3 - 2.0	1.5	159.5	4,466	882	107.0	2,996
Ammonia					392		
Propylene	0.2 - 0.5	0.31	46.5	1,956	417	22.3	939
Propane	0.2 - 1.0	0.47	79.3	3,495	711	33.8	1,491
Hydrocyanic Acid	0.006 - 0.04	0.006	1.1	30	466	0.4	12
Acrylonitrile	0.002 - 0.13	0.0016	4.7	248	10,221	0.1	6
Acetonitrile	0.02 - 0.06	0.054	2.3	95	319	3.9	160
Nitrogen + Argon	78 - 84	80.9	7,394.9	207,056	84,094	5,809.9	162,677
Oxygen	3.0 - 6.8	0.1 - 2.5	489.5	15,664	5,686	60.3	1,931
Water	5.5 - 11.0	13.3	788.4	14,191	3,726	955.3	17,195
NOx		0.0003				TR	1
			9,220.1	258,372	108,532	7,182.6	195,750

(a) Does not include start-up operation.

(b) Based on data from one producer.

(c) Represents average flow during start-up of one reactor in a two reactor system. If other reactor is on-stream, total vent will contain indicated flow plus 50 percent of normal flow shown in preceding column.

2. Product Fractionation Vent

This represents a small stream, which varies greatly in composition, depending upon type of fractionation system used for product recovery. In some cases, this stream consists of the combined vent from several fractionators. Normally this material is sent to an incinerator or flare but at least one manufacturer vents part of this gas, which contains some nitriles (0.0007 tons/ton of acrylonitrile), directly to the atmosphere.

3. Product Storage Vent

Because of the low vapor pressure of acrylonitrile and acetonitrile at ambient temperature (3 - 5 PSI), storage tanks for these two products are directly vented to the atmosphere. In some cases, conservation type vents are employed for safety reasons but they also tend to reduce emissions.

Since HCN is volatile (78° F boiling point), it is stored under positive pressure and generated vapors are cooled by refrigeration for recovery of HCN (-15 to 30° F). Non-condensibles plus associated HCN are normally sent to incineration.

4. By-Product Incineration

In most cases, production of acetonitrile and HCN exceeds demand and excess production is sent to an incinerator. Based upon published data [2,3,4] it is likely that a small portion of the chemically bonded nitrogen contained in the incinerator feed is converted to NOx. Therefore, the quantity of NOx production is related to the amount of by-product HCN and acetonitrile that is burned. This contradicts limited survey data which show NOx emissions to be low (51-1 and 51-2) and independent of feed composition (51-2).

Published data on by-product incineration by one acrylonitrile manufacturer shows that NOx yield is one to three percent of theoretical in their commercial incinerator operating at 1600° F.[18] When similar compounds were burned in a laboratory incinerator, NOx production increased to eight to 17 percent of theoretical. This appears to indicate that peak flame temperature, burner configuration and oxygen diffusion phenomena are all important in determining the amount of NOx produced.

B. Intermittent Air Emissions

1. Process Vent Gas

During reactor start-up, the reactor effluent may by-pass the neutralizer and may be directly vented to the atmosphere. Table AN-4 shows a typical average composition for this vent stream during start-up of one reactor in a two reactor system using Catalyst 21. Actual stream composition changes during the start-up. This operation normally requires a maximum of one hour with one plant start-up every one or two years.

Only one of the plant surveys (51-4) showed an estimate of the amount of particulates emitted in this stream. No data are available regarding the size distribution of these particulates which are catalyst fines that have passed through the reactor cyclones. During normal on-stream operation these fines are removed in the neutralizer and downstream absorber.

2. Emergency Relief

During plant up-set or other emergencies the following streams are occasionally diverted to the flare stack or by-product incinerator:

(a) Propylene Storage

Propylene storage tank relief valves discharge to flare. However, this is an infrequent occurence.

(b) Propylene Feed

Propylene is directed to the flare if the source of heat for feed vaporization is lost and freeze-up of the vaporizer occurs. This happens about once every two years with the flaring lasting about two hours (hourly propylene loss approximately 0.35 tons/ton of acrylonitrile). In addition, during yearly scheduled shut down vaporizers are normally sent to flare. This deliberate shut down results in flaring about 25 percent of the amount of propylene lost during emergency conditions.

(c) By-Product HCN

If by-product HCN is normally marketed, an up-set in the product fractionation system can throw the HCN off specification. In this event the HCN is not reprocessed but is usually sent to an incinerator.

C. Liquid Wastes

1. Neutralizer Effluent

Normally sulfuric acid is used to neutralize the reactor effluent (acetic acid has also been proposed for this operation). A 10 to 20 wt. % ammonium sulfate solution is obtained in the ammonia neutralization and condensation of water from the reactor effluent. Since market demand for ammonium sulfate is low, this stream (0.4 - 3 tons/ton acrylonitrile) is sent to deep well disposal. Several of the plants have by-product incinerators capable of burning some of this material. However, such incineration may result in exceeding emission limitations on sulfur oxides and/or particulates.

2. Product Recovery Waste Water

There are two waste water streams rejected from the product fractionation system. Disposal of one of these streams (one to three tons/ton acrylonitrile) is normally by the same methods used for the neutralizer effluent. This stream is low in total cyanide content and has essentially no acetonitrile. The second stream is much smaller in quantity and contains up to 3 wt. % HCN and 3 to 8 percent acetonitrile.

This reject stream is either incinerated or disposed of via deep well The range in acetonitrile content of this stream depends on whether or not acetonitrile is recovered as a by-product.

D. Solid Wastes

Solid wastes, ranging between 0.0003 to 0.008 tons/ton acrylonitrile, are removed from waste water settling ponds. This sludge consists of catalyst fines and polymers removed in the reactor effluent neutralizer.

In plants employing uranium catalyst, this solid waste is radioactive (approximately two uc/lb.) and disposal is in accordance with AEC regulations. Other types of spent catalyst are sold for metals recovery.

IV. Emission Control Devices and Systems

A. Emission Controls on Main Process Vent

1. Devices Currently Employed

At present most of the U.S. plants do not have any significant emission control facilities on the absorber vent stream. All plants incorporate a mist eliminator in the top of the absorber to prevent liquid carryover to the atmosphere. However, this rather inexpensive device does not reduce hydrocarbon emissions.

2. Combustion Devices (None Currently in use on Acrylonitrile Plants)

The most practical method of reducing the amount of CO and hydrocarbons in the absorber vent gas is by using one of the following combustion devices:

(a) CO-Boiler

Employing a CO-boiler is one of the more efficient methods of removing these contaminates. However, as reported in another volume of this series (Carbon Black - EPA-450/3-73-006a), by-product steam credits can not usually off-set operating costs.

A large amount of steam is presently produced in the conventional acrylonitrile plant by internal coils in the reactors and indirect heat exchange with reactor effluent. This steam is used to drive the air blower and provide process steam requirements. Therefore, most if not all the steam produced in conjunction with any pollution control device will have to be exported. If it is decided to concentrate acetonitrile prior to incineration, about 30 percent of the CO-boiler net steam production could be used for this fractionation; see Section C-1.

Table AN-5 presents a typical material balance for a CO-boiler processing the absorber vent gas from a 200 MM lbs./yr acrylonitrile plant employing Catalyst 41. In order to insure complete combustion of pollutants, the data in Table AN-5 are based on an 1800° F combustion zone temperature and four mol. percent oxygen (dry basis) in the stack gas.

No existing U.S. plant employs CO-boilers or any other combustion device on this vent stream. Therefore, it is difficult to accurately predict equipment performance in this application.

Based upon applications in other areas, the following potential problems exist with off-gas burning in CO-boilers:

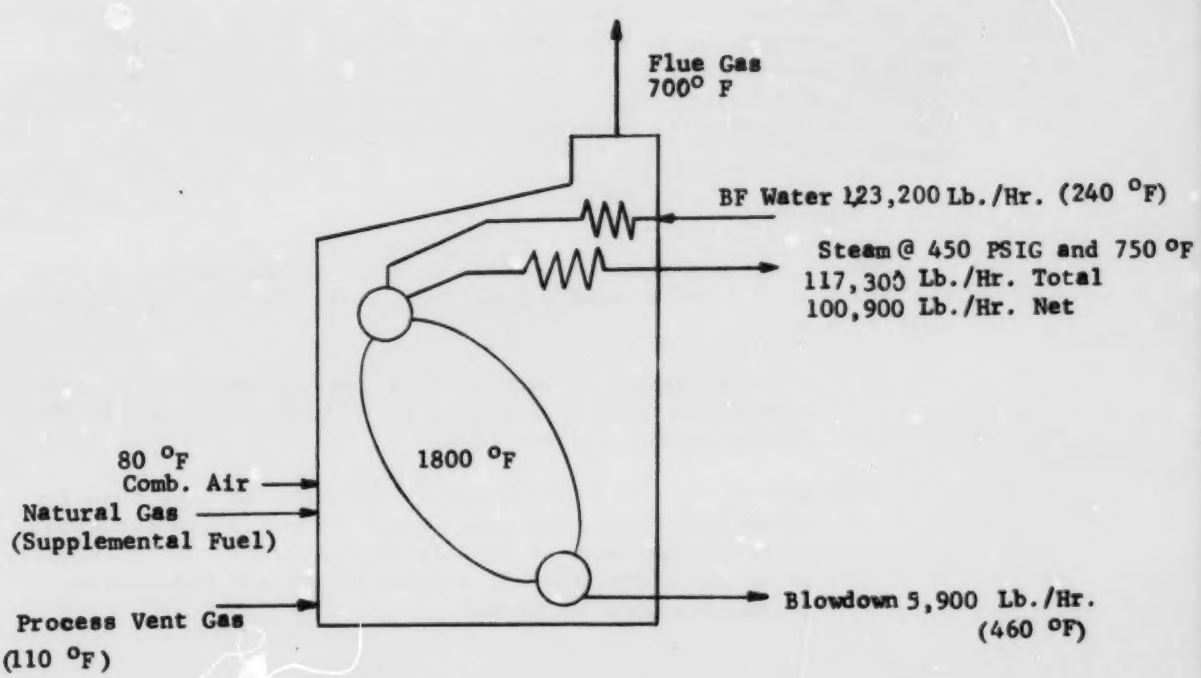
(1) Vent gas is available at low pressure.

(2) Investment for required blowers, large diameter pipes and valves, burning equipment, control systems and steam utilization systems is high.

TABLE AN-5
CO-BOILER EMISSION CONTROL SYSTEM
FOR
200 MM LB./YR. ACRYLONITRILE PLANT
ABSORBER VENT STREAM

OVERALL MATERIAL BALANCE, LB./HR.

Component	Process Vent Gas	Comb. Air	Natural Gas	Flue Gas
Carbon Dioxide	8,342			40,680
Carbon Monoxide	2,966			
Methane			5,858	
Ethane			1,291	
Propylene	939			
Propane	1,491			
Hydrogen Cyanide	12			
Acrylonitrile	6			
Acetonitrile	160			
Nitrogen	162,677	179,598	601	342,900
Oxygen	1,931	54,547		17,514
Water	17,195	3,097		39,558
Nitrogen Oxides				90
Total Lbs./Hr.	195,750	237,242	7,750	440,742
SCFM	45,370			100,550



(3) Because the gas has a low heating value (20 to 40 BTU/Ft.3), 25 to 70 percent of the total heat requirement must be added as supplemental fuel in order to achieve complete combustion.

(4) Flame control is difficult due to low heating value and low level of incandescence, therefore, flame-outs are common.

(b) Thermal Incinerators

Table AN-6 presents a material balance for this type of control device. Data in this table are based on the same combustion zone operating conditions used for the CO-boiler. Heat generated from burning the process vent gas plus feed effluent heat exchange and a small amount of supplemental fuel are required to obtain the desired operating temperature. If heating value of the gas differs from the 24 BTU/Ft.3 used in Table AN-6, heat balanced operation can be obtained by adjusting the amount of supplemental fuel.

Burning of off-gas in a conventional thermal incinerator results in similar burning problems and combustion efficiency anticipated for a CO-boiler.

(c) Incineration plus Steam Generation

Table AN-7 presents a material balance and sketch for a thermal incinerator followed by a waste heat boiler. This combination facility has an emissions control efficiency similar to that of the CO-boiler but does not produce as much steam.

(d) Catalytic Incinerator

A catalytic incinerator could reduce pollutants to similar levels obtained with a thermal unit. The catalytic incinerator would operate at lower temperature (900-1200° F) and, therefore, would probably produce somewhat less NOx. As found in the carbon black in-depth study previously mentioned, catalytic incinerator operating costs would be higher than those projected for a thermal unit.

(e) Flare System

This control device is different from a plume burner in that the plume burner has a self supporting flame. It has the following limitations:

(1) A large amount of supplemental fuel is required to sustain combustion (180 MM BTU/hour with Catalyst 41 or 125 MM BTU/hr. with Catalyst 21).

(2) Efficiency for removal of contaminants is less than for other combustion devices. Based upon qualitative data from similar control devices in the carbon black industry, it is estimated that 90 percent of CO and hydrocarbon pollutants will be burned.

TABLE AN-6
THERMAL INCINERATOR
FOR
200 MM LB./YR. ACRYLONITRILE PLANT
ABSORBER VENT STREAM
OVERALL MATERIAL BALANCE, LB./HR.

Component	Process Vent Gas	Combustion Air	Natural Gas	Flue Gas
Carbon Dioxide	8,342			23,398
Carbon Monoxide	2,996			
Methane			755	
Ethane			167	
Propylene	939			
Propane	1,491			
Hydrogen Cyanide	12			
Acrylonitrile	6			
Acetonitrile	160			
Nitrogen	162,677	81,529	78	244,315
Oxygen	1,931	24,757		12,301
Water	17,195	1,408		24,353
Nitrogen Oxides	1			77
Total Lbs./Hr.	195,750	107,694	1,000	304,444
SCFM	45,370			69,440

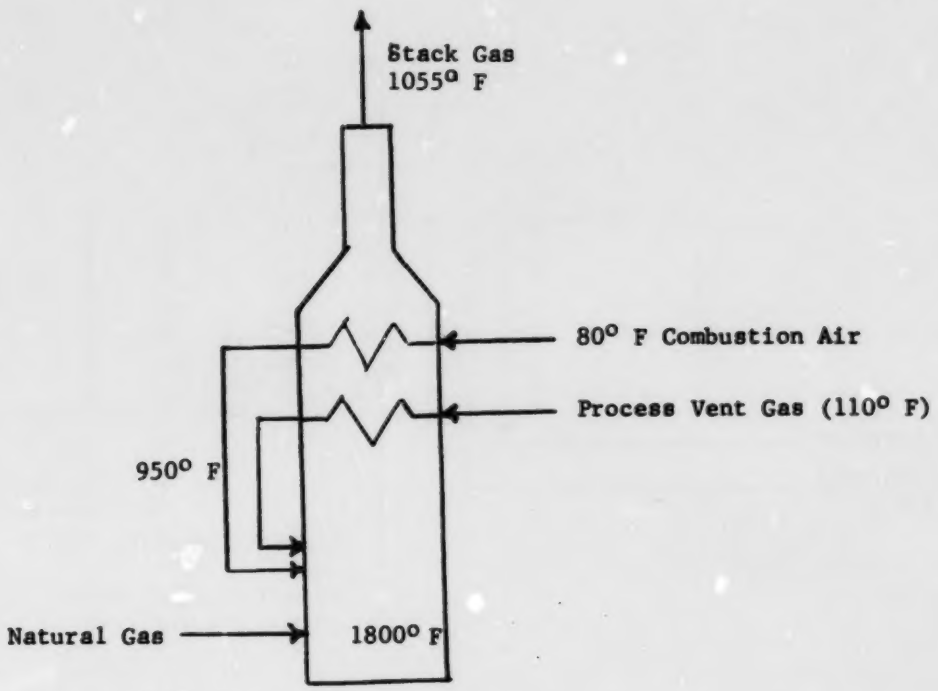
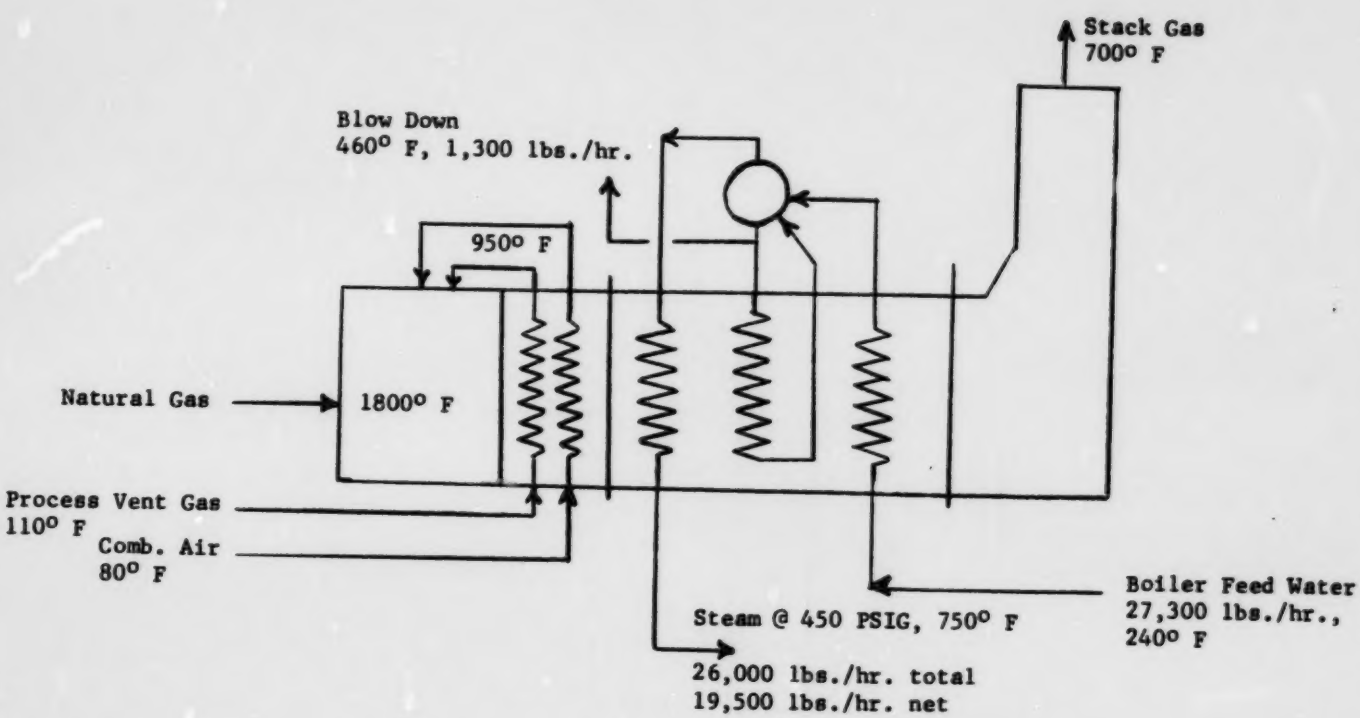


TABLE AN-7
THERMAL INCINERATOR PLUS WASTE HEAT BOILER
FOR
200 MM LB./YR. ACRYLONITRILE PLANT
ABSORBER VENT STREAM
OVERALL MATERIAL BALANCE, LBS./HR.

Component	Process Vent Gas	Combustion Air	Natural Gas	Flue Gas
Carbon Dioxide	8,342			23,398
Carbon Monoxide	2,996			
Methane			755	
Ethane			167	
Propylene	939			
Propane	1,491			
Hydrogen Cyanide	12			
Acrylonitrile	6			
Acetonitrile	160			
Nitrogen	162,677	81,529	78	244,315
Oxygen	1,931	24,757		12,301
Water	17,195	1,408		24,353
Nitrogen Oxides	1			77
Total Lbs./Hr.	195,750	107,694	1,000	304,444
SCFM	45,370			69,440



(3) Improper firing of the burner could result in operating temperatures which favor NOx formation.

(4) Changes in vent gas composition could extinguish the burner if adequate instrumentation is not provided.

(f) Limitations

Most of the above methods of contaminent removal result in a small amount of NOx formation. In addition, if the supplemental fuel contains sulfur compounds some sulfur oxides would also be present in the vent stream.

B. Product Fractionation Vent Gas

Currently this stream is usually sent to a flare stack. None of the surveyed plants have attempted to analyze the flare stack effluent. However, it is estimated that more than 90 percent of the combustibles are burned. Since the quantity of fractionation vent gas is small (Table AN-3, Stream 10), there is little incentive to use a more efficient combustion device.

C. By-Product Disposal

1. Thermal Incineration

All plants surveyed have a thermal incinerator for burning some by-products on a continuous or intermittent basis. At present a major portion of by-product acetonitrile is sent to deep well disposal. Assuming that regulations on water pollution continue to become more stringent, it is likely that in the future other methods for disposal of this chemical will be required.

Approximately 10 percent of by-product HCN is currently sent to deep well disposal and about 40 percent is burned in incinerators.

Polymers and heavy ends recovered in product fractionation section are incinerated, disposed of in deep wells or sent off-site as solid waste.

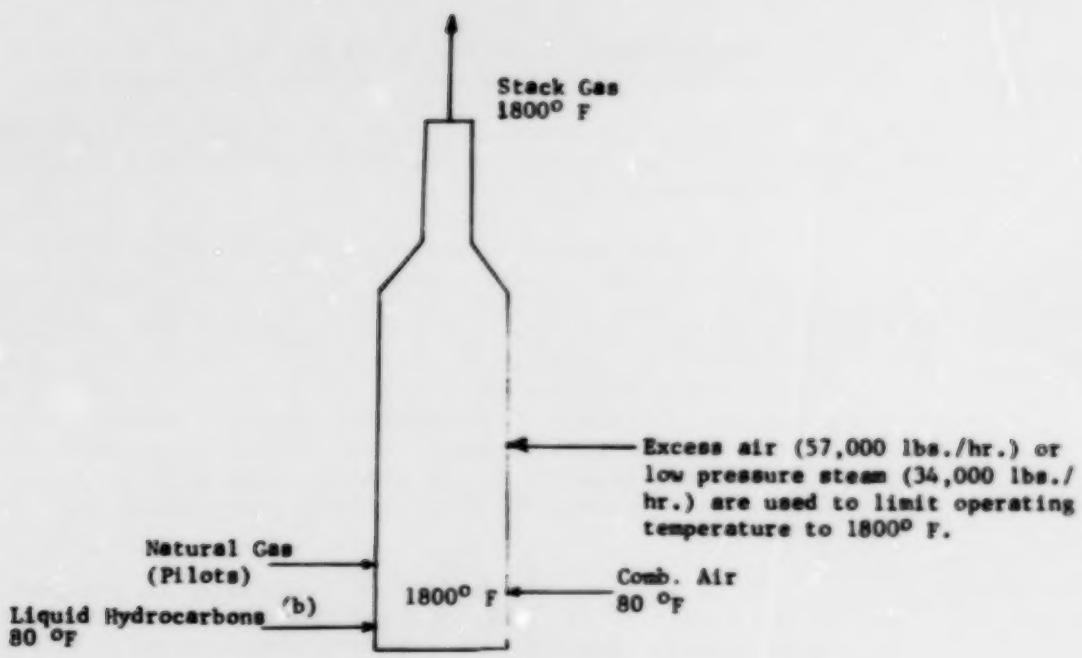
Table AN-8 presents data for a typical plant (200 MM lbs./yr. acrylonitrile production) burning all by-product acetonitrile (2,424 lbs./hr.), heavy ends (200 lbs./hr.) and half (2,119 lbs./hr.) of the by-product HCN in a thermal incinerator. This incineration is self-sufficient in heat and only requires supplemental fuel for pilots. Data in Table AN-8 assumes acetonitrile is recovered as a concentrated liquid in the product fractionation system. Normally, this chemical is sent to deep well disposal, hence little effort is made to separate it from water rejected in the product fractionation section. Under these circumstances, the dilute stream will contain five to 10 percent hydrocarbon.

In most cases, the by-product incinerator is designed to burn dilute acetonitrile (Table AN-1, Stream 9) and the neutralizer waste water stream. However, all plants surveyed normally send both of these water streams to deep well disposal and only burn this material during emergencies, such as injection pump failure (approximately

TABLE AN-8
THERMAL INCINERATOR
FOR
200 MM LB./YR. ACRYLONITRILE PLANT
BY-PRODUCT STREAMS (b)

OVERALL MATERIAL BALANCE, LB./HR.

Component	Hydrocyanic Acid	Acetonitrile	Heavy Ends	Comb. Air	Stack Gas
Hydrogen Cyanide	2,101				
Acrylonitrile	11				
Acetonitrile		2,424	50		
Sulfuric Acid	1				1
Organic Polymers			150		
Carbon Dioxide					9,154
Nitrogen				36,517	38,425
Oxygen				11,087	2,111
Water	6			629	3,160
Nitrogen Oxides					125 (a)
Total LBS./HR.	2,119	2,424	200	48,233	52,976
GPH	370	375	25		
SCFM				10,600	11,500



(a) Based on limited survey data.
(b) Consists of stream 11, half of stream 7 and acetonitrile from stream 9 of Table AN-1.

once a year). Deep well disposal is more economical because of the large amount of heat required to vaporize water and preheat this additional material to combustion zone temperature (1600-1800° F). If both waste water streams in addition to the Table AN-8 hydrocarbon material are charged to the incinerator, approximately 125 MM BTU/hr. of supplemental fuel is required.

Besides requiring more fuel, incinerating the neutralizer effluent increases air emissions. Sulfuric acid is used by virutally all plants for reactor effluent neutralization. Therefore, the neutralizer waste water contains a substantial amount of ammonium sulfate which produces sulfuric acid (about 0.0378 tons/ton of acrylonitrile production when using Catalyst 41) in the incinerator. For this reason neutralizer effluent incineration is not desirable under any circumstances. Tankage or ponds should be available to hold this particular reject stream during emergencies.

Future water pollution regulations may prevent present normal waste water dumping disposal methods. Under these circumstances, steam produced in the absorber vent pollution control system could be used to remove acetonitrile from the product fractionation waste water reject by distillation. It is estimated that about 25,000 lbs./hr. of steam would be required to recover the by-product acetonitrile shown in steam 9 of Table AN-1. The recovered stream would contain about 20 wt. % water and could be burned in the by-product incinerator without requiring any supplemental fuel. The incinerator effluent could be used in a spray drier to evaporate the neutralizer water reject stream for ammonium sulfate recovery.

The effluent NOx concentration shown in Table AN-8 is primarily based on data provided by one acrylonitrile manufacturer (plant 51-1) and is in agreement with published NOx yield figures (two percent of theoretical)[21]. The only other surveyed plant (51-2) that has analyzed this stream reports very low NOx production in the by-product incineration. Insufficient data are available to determine exactly how much NOx is produced. Based upon published data [2,3,4,21] and other information [5], it is likely that a small portion of the chemically bonded nitrogen contained in the feed is converted to NOx. However, it is doubtful if NOx emissions would greatly exceed Table AN-8 values in a properly designed commercial unit operating at 1600-1800° F.

2. Other Combustion Devices

Obviously other types of combustion equipment, not presently employed could be used to burn the by-products. However, most of these would not have the flexibility to economically handle alternative reject streams. For example, if a CO-boiler is used or a waste heat boiler is added to an incinerator, this equipment would have to be designed for maximum heat load. If the product fractionation waste water stream is only sent to the facility on an intermittent basis, economics would not favor providing this heat recovery equipment.

Assuming only the reject hydrocarbons are to be burned, catalytic incineration would be more expensive to operate than a thermal unit. However, if the dilute acetonitrile is to be a continuous feed, operating cost would be less for a catalytic incinerator. This is because the lower catalytic operating temperature (900-1200° F vs.

1800° F) results in lower supplemental fuel requirements. However, before a catalytic unit could be recommended for this service, performance data would be required to determine combustion efficiency for this type of operation.

Plume burners represent a low capital investment combustion device but are not recommended for burning the hydrocarbon reject stream. Inefficient operating of this type of device could permit large emissions of HCN to the atmosphere.

D. By-Product Storage Vent

In acrylonitrile plants where HCN is produced as a marketable by-product, the HCN storage tanks are usually vented to a flare. This small vent stream is primarily nitrogen plus approximately 15 lbs./hour of HCN (for the typical 200 MM lbs/year acrylonitrile plant).

None of the surveyed plants have attempted to analyze the effluent from this flare. Combustion efficiency is probably similar to that obatined with the product fractionation vent flare.

E. Best Pollution Control Systems

The most feasible method of reducing air emissions from existing acrylonitrile plants would be to provide a thermal incinerator on the absorber vent stream.

The best pollution control system for new units would include a thermal incinerator plus a waste heat boiler on the absorber vent. Product fractionation and HCN storage vent gas streams would be flared and by-product hydrocarbons incinerated. If source sampling indicates that by-product incineration in existing plants does not produce significant NOx, it would be desirable to provide a single incinerator for the absorber and by-product hydrocarbon streams.

F. Industry Research Efforts

Current industry effort in air pollution control centers around development of more selective catalysts which will reduce the amount of by-products and increase utilization of ammonia.

V. National Emission Inventory

Based upon the emission factors shown in Table AN-3A, the total approximate emissions from U. S. acrylonitrile plants are as follows (with Catalyst 21):

Component	Average Emission (a) T/T of Acrylonitrile	Total Emissions (b) MM Lbs./Yr.
Hydrocarbons	0.1650	181.5
NOx	0.0050 (c)	5.5
CO	0.1779	195.7
	0.3479	382.7

If Catalyst 41 were to completely replace Catalyst 21 on all current plants, the emission factors would become as follows:

Component	Average Emissions T/T of Acrylonitrile	Total Emissions (b) MM Lbs./Yr.
Hydrocarbons	0.1071	117.8
NOx	0.0050 (c)	5.5 (c)
CO	0.1222	134.4
	0.2343	257.7

Since acrylonitrile production rate is fairly constant throughout the year, there is no seasonal variation in total emissions.

The above data indicate that a reduction of about 30 percent in total air emissions could be achieved by the use of the third generation catalyst. This projection is based on data from a single plant.

(a) Weighted average based on individual plant emission factors and acrylonitrile production.
(b) Based on 550,000 tons/yr. total acrylonitrile production.
(c) Excludes NOx possibly formed in flaring product fractionation and HCN storage tank vent streams. See Section VII.

VI. Ground Level Air Quality Determination

Table AN-3A presents a summary of air emissions data for the various surveyed acrylonitrile plants. This table includes emissions from absorber vent stream, flue gas from incineration of light and heavy end impurities and emissions from flare stack incineration or direct atmospheric venting of non-condensable gases plus minor vapor streams from product fractionation reflux drums, decanters and steam jet vacuum system. Information regarding vapor losses from feed and product storage have not been included. Emissions to the atmosphere from these storage facilities should be low for the following reasons:

(a) Propylene feedstock and by-product HCN storage tanks include refrigeration systems for vapor recovery. Any non-condensibles are normally vented to the incinerator.

(b) Acrylonitrile product and by-product acetonitrile have relatively low vapor pressure (3-5 psi) at normal storage tank operating temperatures. These tanks usually contain conservation type vents with vacuum breakers in order to minimize losses.

Table AN-3A provides operating conditions and physical dimensions of the various vent stacks. The EPA may use this information together with the air emission data to calculate ground level concentration for latter reporting.

The data of Table AN-3A were collected while the surveyed plants were using Catalyst 21. One plant has changed (completely) to Catalyst 41 and most of the other plants are in the process of a gradual changeover. Hence, data modifications will probably be in order at the time when the EPA calculates ground level concentrations.

VII. Cost Effectiveness of Controls

Table AN- 9 presents a cost analysis for the alternate methods of reducing air pollution from the various vents. Economic data presented in this table are for a new plant producing 200 MM lbs./yr. of acrylonitrile and are based on the following (using Catalyst 41):

A. Investment

Purchase cost of boilers was obtained from current vendor quotes for similar packaged type units. Published data [2], were used to determine incinerator costs and investment data provided in various plant surveys were employed to estimate installed costs for plume burners and flare stacks.

Installation costs for the various packaged units are estimated values based on previous experience in plant construction. A major portion of this cost represents construction labor.

B. Operating Expense

1. Depreciation - 10 year straight line.

2. Interest - 6% on total capital

3. Maintenance - Set at 4% of investment for boilers and 3% for incinerators. Maintenance costs for other control devices are based on data provided in plant surveys.

4. Labor - One man per shift used for direct fired boilers and 6 hrs./day for waste heat boilers. Virtually no operating labor is required for incinerators.

5. Utilities - Unit costs are based on typical values for the Gulf Coast area. (1973)

Except for plume burners and flare stacks, all emission control devices listed require induced or forced draft blowers. Power requirements for these blowers are based on the following assumed system differential pressures:

	ΔP in. H_2O
CO-Boiler	14
Thermal Incinerator	6
Thermal Incinerator plus Waste Heat Boiler	14

In the case involving CO-boilers for absorber vent emissions control, investment costs are based on providing a 100% spare boiler. This provides a more dependable steam supply.

Table AN-9 indicates that employing dual CO-boilers is not an economical method of reducing emissions. However, if a stand-by boiler is not required, this type of control device is about as economical to operate as other combustion devices and represents one of the most efficient methods of reducing combustable emissions.

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TABLE A-9

COST EFFECTIVENESS FOR ALTERNATE EMISSION CONTROL DEVICES

BASED ON 20 TONS/S.D. ANHYDROUS AMMONIA PRODUCTION

Sheet 1 of 3

Stream: ABSORBER VENT GAS (a)

Type of Emission Control Device	CO-Boiler	Thermal Incinerator	Thermal Incinerator	Waste Heat Boiler	Flare System
Number of Units	2	1	1	1	1
Capacity of Each Unit, %	100	100	100	100	100
Feed					
Total Flow, Lbs./Hr.		195,750			
SCFM		45,340			
Composition, Tons/Ton AN					
Hydrocarbons		0.106			
Particulates					
SOx					
Carbon Monoxide		0.122			
Combined Effluent					
Total Flow, Lbs./Hr.	440,742	304,444	304,444		60,000
SCFM	100,550	69,440	69,440		
Composition, Tons/Ton AN					
Hydrocarbons					0.011
Particulates					
NOx	0.0037	0.0031	0.0031		0.0025
SOx					
Carbon Monoxide					0.012
Emissions Control Efficiency (e)					
CCR	100	100	100		90
SERR	98	98	98		89
Investment, $					
Purchased Cost	800,000 (a)	175,000	175,000	165,000 (a)	
Installation	1,200,000	175,000	175,000	245,000	
Total Capital	2,000,000	350,000 (b)	350,000 (b)	410,000	150,000 (d)
Operating Cost, $/Yr.					
Depreciation (10 years)	200,000	35,000	35,000	41,000	15,000
Interest on Captical (6%)	120,000	21,000	21,000	24,600	9,000
Maintenance	80,000 (4%)	10,500 (3%)	10,500 (3%)	16,400 (4%)	8,000
Labor, $4.85/Hr.	39,600	1,000	1,000	10,000	
Utilities					
Power, 1¢/KWH		4,300	4,300		
Fuel, 40¢/MM BTU (c)	497,100	64,100	64,100		587,500
Boiler Feed Water, 30¢/M. Gal.	36,200			8,000	
Total Utilities	533,300	68,400	68,400	8,000	587,500
Total Operating Costs	972,900	135,900	135,900	100,000	619,500
Steam Production, 75¢/M. Lbs. (450 PSIG, 750° F)	(617,500)			(119,300)	
Total Annual Cost	355,400	135,900	135,900	(19,300)	619,500
			116,600		

AN-32

TABLE AN-9 CONTINUED
COST EFFECTIVENESS FOR ALTERNATE
EMISSION CONTROL DEVICES
BASED ON 200 MM LBS./YR. ACRYLONITRILE PRODUCTION

Stream	Product Fractionation Vent (e)	By-Product Disposal (o)		HCN Storage Tank Vent (o)
Type of Emission Control Device	Flare	Thermal Incinerator		Flare
Number of Units	1	1		1
Capacity of each Unit,	100	100		100
Feed				
Total Flow, LBS./HR.	423			
SCFM	70	4,743		110
Composition, Tons/Ton AN				25
Hydrocarbons	0.004			
Particulates		0.1933		0.0006
NO_x				
Carbon Monoxide				
Combined Effluent				
Total Flow, LBS./HR.		52 976		
SCFM	600	11,500		170
Composition, Tons/Ton AN				
Hydrocarbons	0.0004			0.00006
Particulates				
NO_x	0.0014			0.0003
SO_x		0.005 (j)		
Carbon Monoxide				
Emissions Control Efficiency (e)				
CCR	90	100		90
SERR	72	99 (j)		65
Investment, $				
Purchased Cost		175,000 (b)	110,000 (b)	
Installation		175,000	110,000	
Total Capital	75,000	350,000 (g,l)	220,000 (b)	20,000 (m)
Operating Cost, $/Yr.				
Depreciation (10 years)	7,500	35,000	22,000	2,000
Interest on Capital (6%)	4,500	21,000	13,200	1,200
Maintenance	3,500	7,000 (2%)	4,400 (2%)	1,000
Labor, $4.85/Hr.	1,500	3,300	3,300	1,000
Utilities				
Power, 1¢/KWH		2,400	2,400	
Fuel, 40¢/MM BTU (c)	3,500	2,000	2,000	
Boiler Feed Water, 30¢/M. GAL.				1,200
Total Utilities	3,500	4,400 (k)	4,400 (k)	1,200
Total Operating Costs	20,500	70,700	47,300	6,400
Steam Production, 75 /M. LBS. (450 PSIG, 750° F)				
Total Annual Cost	20,500 (m)	70,700	47,300	6,400 (m)

TABLE AN-9
COST EFFECTIVENESS FOR ALTERNATE
EMISSION CONTROL DEVICES
BASED ON 200 MM LBS./YR. ACRYLONITRILE PRODUCTION
FOOT NOTES

(a) Based on vendor quote for similar unit.

(b) Afterburner systems study by Shell Development Co. for EPA (Contract EHSD 71-3).

(c) It is likely that future fuel costs will be considerably higher than used in this tabulation.

(d) Based on investment data provided by carbon black manufacturers for similar type of equipment.

(e) See Appendix III for discussion and definition of efficiency as used here.

(f) Flow rates and utilities exclude waste water processing.

(g) Excess capacity available for processing all waste water streams.

(h) Excess capacity for product fractionation waste water disposal but excludes capacity for neutralizer effluent.

(j) To be confirmed by source testing.

(k) Excludes utilities for burning waste water streams.

(l) Excludes incinerator effluent scrubber

(m) Based on cost data provided by acrylonitrile manufacturer's.

(n) Based on use of Catalyst 41.

(o) Based on use of either Catalyst 21 of 41.

Based on published information for burning fuels containing nitrogen, it has been assumed that 50 percent of the chemically bonded nitrogen in the CO-boiler feed goes to NOx with complete combustion of hydrocarbons and CO.

A thermal incinerator with feed and air preheat followed by a waste heat boiler produces less steam for export but is more economical to operate than the direct fired boiler which requires more fuel. It is assumed that absorber vent gas emissions from this unit would be similar to those predicted for CO-boilers.

Thermal incineration of the process vent gas without steam generation has a somewhat higher operating cost than the unit including a waste heat boiler. However, this device could be incorporated in existing or new plants where steam can not be exported to other process areas.

Flaring of the absorber vent is impractical because of the large fuel requirement.

It should be noted that economic data presented for the various combustion devices are based on processing a typical absorber vent gas having a heating value of 24 BTU/SCF. If for a particular feedstock (less propane), air to hydrocarbon feed ratio, and catalyst (high selectivity), the vent gas heating value is lower than this typical figure, it would be necessary to increase supplemental fuel usage in the combustion devices. For higher heating value gases, less fuel and/or reduced feed-effluent heat exchange would be required.

Cost for installing the various absorber vent pollution control equipment in existing plants would be about the same or only slightly higher than the figures shown in Table AN-9. The actual cost differential would largely depend on space availability and its location relative to associated process equipment.

Table AN-9 includes economics for flaring the product fractionation and HCN storage tank vents plus thermal incineration of the by-product acetonitrile, heavy ends, and half the by-product HCN (see Table AN-8). The by-product incineration data are based on limited emissions data provided by the acrylonitrile manufacturers. However, if source testing indicate large amounts of NOx production for this incineration, additional downstream processing may be required.

By-product incinerator investments are shown for units sized to burn reject liquid hydrocarbons plus part or all of the process waste water. Incinerator utilities shown in Table AN-9 assume neither waste water stream is being fed to the unit. It should be noted that it is not advisable to burn the neutralizer effluent stream because of resulting air emissions. If this stream is to be incinerated more often than just during short term emergencies, it would be necessary to add a scrubber on the incinerator effluent. Cost of this scrubbing facility has not been included in the economics.

Emission control efficiencies shown for flaring the product fractionation and HCN storage tank vents are based on assuming 90 percent combustion of combustibles with 50 percent conversion of chemically bonded nitrogen to NOx (95 mol. % NO and 5% NO_2). Plant survey data in Table AN-3A fail to show significant quantities of NOx in the flare effluents. It should be noted that none of the surveyed plants actually analyze these streams. Therefore, even though the total NOx emission based on the above assumptions is

significantly higher than the reported values (0.0035 T/T of AN versus 0.00002 T/T for plant 51-4), there are no analytical data to indicate which of these two values is a closer representation of the actual emissions.

Obviously, with tabulations such as presented in Table AN-9, the reader can make a variety of adjustments to satisfy specific accounting techniques or technical standards. Thus unit costs can be modified to be appropriate to local situations or to account for future escalation. Similarly, different combinations of equipment can be considered. For example, if only a single CO-boiler were employed, the investment would drop to about $1,000,000 and the annual operating cost would be reduced to $155,400 per year, assuming that the reliability of steam export could assure the $617,500 estimated income.

VIII. Source Testing

It is recommended that source sampling should be performed on the by-product incinerator feed and effluent streams at the 51-1 acrylonitrile plant. This is the only surveyed plant which has sample taps available for convenient effluent sampling. If possible, feed quantity and composition should be varied in order to determine effect on NO_x emissions.

Plant 51-1 does not send the neutralizer waste water stream to incineration. If combustion products from ammonium sulfate incineration are to be determined, similar testing of either 51-2 or 51-3 incinerator would be necessary. If it is decided to source test the by-product incinerator in either of these latter two plants, samples should be obtained with and without the neutralizer waste stream incineration.

It is also recommended that source sampling of the absorber vent stream from plant 51-4 should be considered. This represents a fairly new plant which shows average emissions. Since absorber emissions from the various units do not vary over a wide range, it may be decided that source sampling of this stream is not required.

IX. Industry Growth Projection

The U. S. annual acrylonitrile production is estimated to increase to 3.7 billion pounds by 1985, see Figure AN-2.

Approximately half of all acrylonitrile produced is used in the production of acrylic fibers. Demand in this area is expected to increase about 12% per year during the next decade as synthetic fibers continue to gain wider acceptance in wearing apparel and carpet manufacture.

The next largest use of acrylonitrile is in the production of plastics. Plastic manufacture consumes about 15% of U. S. acrylonitrile production and the use of these acrylonitrile base resins is growing faster than that for acrylic fibers. Increased utilization of plastics in automobiles could greatly expand acrylonitrile requirements in this area.

Acrylonitrile is also used in production of oil resistant elastomers, adiponitrile, acrylamide and other small volume chemicals.

Approximately 20% of U. S. acrylonitrile is exported. However, as more larger foreign plants are built, these exports are expected to decline.

The projected increase in acrylonitrile production will require the construction of approximately 13 new plants between 1972 and 1985, based on an average plant capacity of 200 million pounds per year acrylonitrile production. It is anticipated that most if not all of these plants will incorporate the Sohio type of process. It is doubtful that a new more economical process will be developed during this period.

About 45 percent of the cost of manufacturing acrylonitrile is due to the cost of propylene feed. Therefore, acrylonitrile selling price is greatly influenced by raw material availability. The cost of propylene in the U. S. is expected to increase due to increased oil costs and as follows:

A. Increasing pressure to improve octane ratings of gasolines without increasing lead content will probably mean increased consumption of propylene for alkylate production.

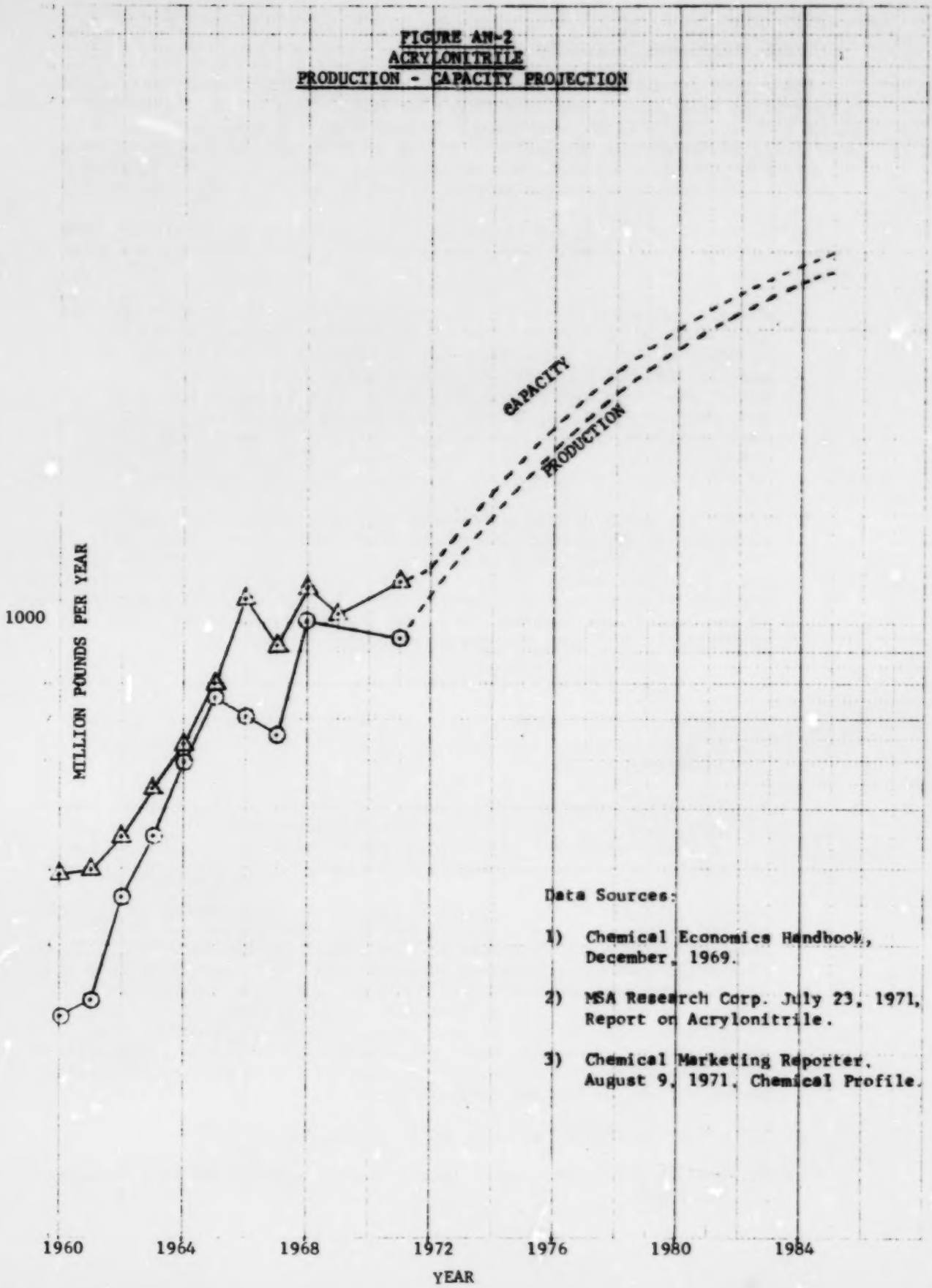
B. Other chemicals such as isopropanol, propylene oxide, polypropylene and cumene which are produced from propylene, represent fast growing petrochemicals which will compete for available feedstock.

C. Availability of refinery propylene is decreasing because of increased use of hydrocrackers, which have low olefin yields, and by the use of zeolite catalysts in cat crackers which result in lower propane and propylene production.

D. By-product propylene production by U. S. ethylene plants is limited by nature of the raw materials employed. Naphtha is generally unavailable in the U. S. as a chemical feedstock because of the high demand for gasoline. Naphtha feed yields considerably more propylene in an ethylene unit than is obtained from propane or ethane feedstock.

Unless similar developments cause the same anticipated propylene increase in Europe, U. S. propylene exports will terminate and may result in some importation of acrylonitrile to meet future product demands. Anticipated escalation in cost of other raw materials, particularly ammonia, may also necessitate acrylonitrile price increases.

FIGURE AN-2
ACRYLONITRILE
PRODUCTION - CAPACITY PROJECTION



Data Sources:

1) Chemical Economics Handbook, December, 1969.

2) MSA Research Corp. July 23, 1971, Report on Acrylonitrile.

3) Chemical Marketing Reporter, August 9, 1971, Chemical Profile.

X. Plant Inspection Procedures

Plant inspections will be conducted by the appropriate authorities, either on a routine basis, or in response to a complaint. Usually the inspecting agent will only be able to make visual observations. In some instance, monitoring equipment may be available on the absorber vent or reactor effluent It should be possible to sample the absorber vent stack through an accessible sample point. This also applies to some of the by product incinerator stacks.

If the inspector has reason to suspect that emissions are excessive, some factors that he should consider and/or discuss with plant officials are itemized below:

A. Normally during start-up of individual reactors, the reactor effluent is allowed to by-pass the neutralizer and absorber column and is directly vented to the atmosphere. A record should be kept as to when and for how long this by-passing occurs. Obviously, an effort should be made to minimize this direct venting of catalyst and reaction products. Process economics as well as air pollution considerations dictate that safeguards should be taken to prevent inadvertent opening of the by-pass valves. A discernible HCN odor in the absorber off-gas could indicate a leaking by-pass valve.

B. Proper operation of the neutralizer and water absorber columns are necessary to limit emissions in the absorber vent gas. This vent stream should be essentially odorless and have the appearance of steam with no residual plume. In addition to making these observations, the control agent must be aware of operating and physical characteristics of the neutralizer and absorber. The inspector should be aware that excessive process vent gas emissions could be caused by:

   1. Water flow rates to both towers being less than design values.

   2. Temperature and pressure of feed gas plus process side pressure drop across the towers being different than normal plant operating and design values.

   3. Temperature profile in top section of absorber being higher than design value. High temperatures which cause excessive carryover of hydrocarbons can result from either inadequate cooling of the absorption water or excessive tower feed.

C. Proper operation of the by-product incinerator is essential in limiting air emissions. A visual check of the incinerator stack gas should be made. A smoky stack indicates malfunctioning of the combustion process. Smoke-free combustion requires adequate time, good turbulence in mixing the fuel and air, and sufficient temperature for the reaction to proceed to completion and produce the desired products of oxidation. If malfunctioning of the incinerator is suspected, log data on the composition of stack gas should be reviewed, if available. Variance in analytical results or general malfunction can usually be attributed to one or more of the following factors:

   1. Burner in combustion zone not in design operation.

   2. Process hydrocarbon waste feeds, atomizing steam and/or air valves not open.

3. Combustion zone temperature not in design range.

4. The quantity of excess air may be different than design. This might be determined by checking the air flow chart or measuring the temperature of stack gases.

5. Variation in incinerator feed composition and flow rate.

The following measures are normally recommended by manufacturers as methods to improve performance of a smoky incinerator.

1. Usually smoke results from low combustion zone temperature or improper fuel to air ratio. If combustion zone temperature is low, consider reducing the amount of excess air or increase supplemental fuel. Variation in overall feed composition could also result in low operating temperatures. For example, if the feed contains a large quantity of water, the combustion temperature could be quenched.

2. If operating temperature appears adequate and furnace still smokes, it may be necessary to increase air rate to the incinerator in order to insure complete combustion.

D. The above comments regarding the by-product incinerator also apply to any incinerator provided on the absorber or other vent streams.

E. A visual check should be made of flare stacks to determine opacity.

XI. Financial Impact

All of the economic projections in this section are based on the use of Table AN-1, Material Balance with raw material requirements and absorber vent gas composition revised to reflect the use of the latest catalyst (Catalyst 41).

Table AN-10 presents economics for acrylonitrile manufacture in a typical 200 MM Lbs./Yr. plant that incorporates incineration of all by-product HCN and acetonitrile plus light and heavy ends from acrylonitrile fractionation.

Table AN-10 also presents economic data for the same unit assuming by-product HCN and acetonitrile can be marketed at about 40 percent of the normal selling price for these chemicals.

Table AN-10 shows that, based on 1973 cost/price levels, the manufacture of acrylonitrile appears to be fairly profitable if by-products can be marketed. About 8.5 percent return on investment is projected assuming no by-product value and 14 percent ROI with the proposed by-product credit.

Table AN-11 shows estimated economics for producing acrylonitrile in an existing plant modified to reduce emissions. The modification consists of adding an incinerator for burning the absorber vent stream. Table AN-11 also provides economics for producing acrylonitrile in a new most feasible unit. This plant includes the same type of equipment employed in the modified existing facility. In addition, a waste heat boiler is included on the absorber vent gas incinerator effluent stream for steam generation.

The economic data indicate about a 0.06¢/lb. increase in acrylonitrile production cost for both the modified existing and new most feasible units. Assuming an acrylonitrile selling price of 12¢/lb., this corresponds to a three percent reduction in profit and reduces return on investment to about eight percent.

It was deemed unnecessary for the purpose of this study to perform a sensitivity analysis with the data of Table AN-11 because the pollution control equipment capital is only about four percent of the total plant investment and the total increase in acrylonitrile cost is less than one percent.

Table AN-12 presents pro-forma balance sheets for the above cases which assume no credit for by-products. It was assumed in developing these asset and liability positions that the acrylonitrile selling price would be held constant and the small increase in total production costs would be taken out of the profit margin in order to maintain sales at a peak level. Capital requirement for the most feasible new plant is about $760,000 higher than for an existing type plant.

In addition to the financial impact, one should also evaluate the overall environmental impact of the most feasible method of emission control described in this report. A prime factor for consideration in this evaluation is the effect on fuel requirements. If the absorber vent gas is burned without waste heat recovery in all future plants, the incremental increase in fuel requirement will be equivalent to about five billion standard cubic feet per year of natural gas by 1985. This increase could be eliminated by using effluent steam generation for heat recovery.

TABLE AN-10
ACRYLONITRILE MANUFACTURING COST
FOR A TYPICAL
EXISTING 200 MM LB./YR. FACILITY

	WITHOUT BY-PROD. CREDIT		WITH BY-PRODUCT CREDIT	
DIRECT MANUFACTURING COST	¢/LB.	$/YR.	¢/LB.	$/YR.
Raw Materials				
90% Propylene @ 2.8 ¢/lb.	3.99			
Ammonia @ 1.5 ¢/lb.	0.74			
Sulfuric Acid @ 1.5 ¢/lb.	0.06			
Catalyst and Chemicals	0.50			
Labor (8 men/shift @ $4.85/hr.)	0.17			
Maintenance (5% of investment)	0.60			
Utilities	0.90			
	6.96		6.96	
INDIRECT MANUFACTURING COST				
Plant Overhead (110% of labor)	0.19		0.19	
FIXED MANUFACTURING COST				
Depreciation (10 years)	1.20			
Insurance & Property Taxes (2.3% of Inv.)	0.28			
	1.48		1.48	
MANUFACTURING COST	8.63		8.63	
GENERAL EXPENSES				
Administration (3% of manufacturing cost)	0.26			
Sales (1% of manufacturing cost)	0.09			
Research (2% of manufacturing cost)	0.17			
Finance (6% of investment)	0.72			
	1.24		1.24	
Total Cost	9.87	19,740,000	9.87	19,740,000
PRODUCT VALUE				
Acrylonitrile @ 12¢/lb.	12.00	24,000,000	12.00	24,000,000
HCN @ 4¢/lb.			0.69	1,380,000
Acetonitrile @ 7¢/lb.			0.69	1,380,000
Total	12.00	24,000,000	13.38	26,760,000
Profit before taxes	2.13	4,260,000	3.51	7,020,000
Profit after 52% tax	1.02	2,045,000	1.68	3,370,000
Cash flow		4,445,000		5,770,000
ROI (NPAT x 100/Investment)	8.52%		14.04%	

TABLE AN-11
ACRYLONITRILE MANUFACTURING COST (a)
FOR A TYPICAL
200 MM LB./YR. FACILITY
WITH ADDITIONAL EMISSION CONTROLS

Type of Plant	Modified Existing Plant (c)		New Plant (d)	
DIRECT MANUFACTURING COST	¢/LB.	$/YR.	¢/LB.	$/YR.
Raw Materials				
90% Propylene @ 2.8¢/lb.	3.99		3.99	
Ammonia @ 1.5¢/lb.	0.74		0.74	
Sulfuric Acid @ 1.5¢/lb.	0.06		0.06	
Catalyst and Chemicals	0.50		0.50	
Labor	0.17		0.18	
Maintenance	0.61		0.61	
Utilities	0.93		0.88 (b)	
	7.00		6.96	
INDIRECT MANUFACTURING COST				
Plant Overhead (110% of labor)	0.19		0.19	
FIXED MANUFACTURING COST				
Depreciation (10 years)	1.22		1.24	
Insurance & Property Taxes (2.3% of Inv.)	0.28		0.28	
	1.50		1.52	
MANUFACTURING COST	8.69		8.67	
GENERAL EXPENSES				
Administration (3% of manufacturing cost)	0.26		0.26	
Sales (1% of manufacturing cost)	0.09		0.09	
Research (2% of manufacturing cost)	0.17		0.17	
Finance (6% of investment)	0.73		0.74	
	1.25		1.26	
Total Cost	9.94	19,880,000	9.93	19,860,000
Selling Price	12.00	24,000,000	12.00	24,000,000
Profit before taxes	2.06	4,120,000	2.07	4,140,000
Profit after 52% tax	0.99	1,978,000	0.99	1,987,000
Cash flow		4,413,000		4,463,000
ROI (NPAT x 100/Investment)	8.12%		8.03%	

(a) No credit for by-products.
(b) Assumes 0.06¢/lb. credit for steam produced in pollution control waste heat boiler.
(c) Includes absorber vent gas incinerator.
(d) Includes absorber vent gas incinerator plus waste heat boiler.

TABLE AN-12
PRO-FORMA BALANCE SHEET
200 MM LB./YR. ACRYLONITRILE MANUFACTURING FACILITY
(NO CREDIT FOR BY-PRODUCTS)

TYPE OF PLANT	EXISTING	EXISTING WITH INCINERATOR	NEW WITH INCINERATOR AND WASTE HEAT BOILER
Current Assets			
Cash (A)	$ 1,438,300	$ 1,448,300	$ 1,445,000
Accounts Receivable (B)	2,000,000	2,000,000	2,000,000
Inventories (C)	1,974,000	1,988,000	1,986,000
Fixed Assets			
Plant	24,000,000	24,350,000	24,760,000
Buildings	100,000	100,000	100,000
Land	50,000	50,000	50,000
Total Assets	$29,562,300	$29,936,300	$30,341,000
Current Liabilities (D)	$ 1,278,300	$ 1,285,000	$ 1,278,300
Equity & Long Term Debt	28,284,000	28,651,300	29,062,700
Total Capital	$29,562,300	$29,936,300	$30,341,000

(A) Based on one month's total manfacturing cost.
(B) Based on one month's sales.
(C) Based on 20 MM lbs. of product valued at total cost.
(D) Based on one month's total cost less fixed manufacturing and finance costs.

XII. Cost to Industry

In the typical present day plant depicted in Table AN-10, approximately two percent of the plant investment is directly attributed to cost of air pollution equipment. This expenditure plus associated operating costs equals less than one percent of the acrylonitrile total production cost (0.05¢/lb.). The following items are included in this cost:

A. Flare for various product fractionation vent streams.

B. By-product incinerator.

C. HCN storage tank vent flare.

As noted in Section XI, the proposed most feasible modification of existing acrylonitrile plants results in only a slight increase in production cost (0.07¢/lb.). Therefore, the addition of absorber vent gas incinerators to existing plants should not cause any significant economic problems to the industry. The total investment cost for modifying all U.S. acrylonitrile plants to burn absorber off-gas in thermal incinerators would be approximately $2,000,000.

In the "most feasible new plant" presented in Table AN-11, air pollution control equipment represents about five percent of total plant investment. The resulting total production cost will be about 0.06¢/lb. higher than for the present day typical unit. The costs involved in the pollution control should not reduce growth in demand for acrylonitrile.

Assuming all new plants built between now and 1985 incorporate this type of air pollution control equipment, the total incremental capital cost will be about $10,000,000.

The projected effect of the above expenditures on future air emissions is shown in Table AN-13.

TABLE AN-13
ESTIMATED 1985 AIR EMISSIONS (A)
FOR
ALTERNATE CONTROL SYSTEMS

Type of Pollution Control	Typical Present System			Most Feasible Modifications (D) Existing Plants		New Plants		Total		
Acrylonitrile Production, (B) Tons/Yr.	1,850,000			550,000		1,300,000		1,850,000		
Pollutant	Average Emissions T/T	Total Emissions MM Lbs./Yr.	Weighted Emissions	Average Emissions T/T	Total Emissions MM Lbs./Yr.	Average Emissions T/T	Total Emissions MM Lbs./Yr.	Average Emissions T/T	Total Emissions MM Lbs./Yr.	Weighted Emissions
Hydrocarbon	0.1071	396.3	31,700	0.0005	0.6	0.0005	1.3	0.0005	1.9	150
NOx	0.0067	24.8	990	0.0098	10.8	0.0098	25.5	0.0098	36.3	1,450
CO	0.1222	452.1	450							
	0.2360	873.2	33,140 (C)	0.0103	11.4	0.0103	26.8	0.0103	38.2	1,600 (C)

(A) Based on all plants using Sohio Catalyst 41.

(B) Estimated production in 1985.

(C) Significant Emission Index, which is based on the following weighting factors: Hydrocarbon = 80, NOx = 40 and CO = 1 (see Appendix II for explanation).

(D) Assumes all existing plants modified and new plants built to incorporate thermal incinerators on absorber vent stream. New plants include a waste heat boiler.

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XIII. Emission Control Deficiencies

Technical deficiencies which hinder reducing the level of emissions include the following:

A. Process Chemistry and Kinetics

Production of acrylonitrile is a catalytic ammoxidation reaction. The amount of acrylonitrile produced is influenced by relative concentration of feed components, reactor residence time, operating temperature and pressure.

1. Reactor Feed

(a) Propylene

Impurities in the propylene feed with less than four carbon atoms are unaffected in the reactor and are primarily rejected in the absorber off-gas. Heavier impurities react forming undesirable by-products. Therefore, in order to minimize air pollution and maximize productivity it is desirable to limit impurities. Feed should also be sulfur free in order to prevent catalyst deterioration.[14]

If an incinerator is provided on the absorber vent stream, there is less incentive to limit ethane and lighter impurities in the propylene feed. In addition to enhancing incinerator operation without hurting production, lower purity propylene could represent a cheaper feedstock.

(b) Ammonia

Excess ammonia feed to the reactor is necessary to limit formation of non-selective products (aldehydes, HCN and carbon dioxide).[15] In addition to improving acrylonitrile selectivity this makes product recovery easier. However, the excess ammonia has to be neutralized prior to product recovery and this neutralization normally produces an unwanted waste product.

(c) Oxygen Concentration

All Sohio acrylonitrile plants use air as a source of oxygen. This results in a large volume of nitrogen being vented which dilutes other emissions. Because of this dilution, it is more difficult and expensive to control the quantity of these emissions.

2. Reactor Operating Conditions

Reactor operating conditions influence propylene conversion rate and to a certain extent the quantity of non-selective products produced in the reactors. Since unconverted propylene is lost in the absorber vent stream, reactor operating conditions are adjusted to obtain high propylene conversion and maximum acrylonitrile production.

3. Catalyst

The type of catalyst employed greatly influences the amount of by-products produced and acrylonitrile productivity. Even

with the most selective catalyst currently employed, by-product production exceeds market demand. This results in disposal problems for these chemicals.

B. Process Equipment and Operations

1. Reactors

The chemical reaction for acrylonitrile production is highly exothermic. Partly for this reason, fluidized reactors with internal cooling coils are employed. This type of reactor results in some catalyst carry over in the effluent stream. However, this catalyst (0.001 T/T of AN) is only emitted to the atmosphere during short time periods following reactor start-ups when the neutralizer and absorber tower may be by-passed.

2. Neutralizer

Sulfuric acid is used to neutralize excess ammonia. This leads to a disposal problem for the resulting by-product ammonium sulfate.

C. Control Equipment and Operations

The proposed incineration of the absorber vent gas, is the best method of reducing air emissions from this stream. The deficiency in this treatment is that it results in production of some NO_x from nitrogen compounds in the vent gas and consumes additional fuel.

There is some question as to how much NO_x is produced in the by-product incinerator. If these emissions exceed air pollution limits, adjustment in the incineration operation or additional treatment of the flue gas for removal of contaminants would be required. See Section XIII-C of Report No. EPA 450/3-73-006a for a description of alternative treatment methods.

XIV. Research and Development Needs

If the technology deficiencies discussed under Section XIII are to be overcome, additional R & D is desirable in the following areas:

A. Existing Plants

1. Improved Catalyst

It would be desirable to have a more selective catalyst in order to pro u e less unwanted by-products and improve utilization of ammonia.

Published data for catalyst used in new Montecatini Edison process shows less by-product HCN and acetonitrile yield for a given acrylonitrile production than is obtained for the Sohio catalysts.[9,10] Since the type of reactor and its operating conditions are similar for both processes, it should be possible to further reduce these particular by-products in the Sohio process. Catalyst development work in this area can best be handled by the process licensor, as has been demonstrated by Sohio's past development of Catalyst 21 and their recent work on Catalyst 41.

B. New Plants

In addition to the above R & D area which has appliation to both new and existing plants, the following items would require new facilities for utilization of gained technology:

1. Source of Oxygen

A combination of pure oxygen feed in place of air and recycle of vent gas to the reactors could reduce net emissions and improve feed utilization. If the absorber vent gas is partially recycled, it is not as critical to maintain high propylene conversion rates. Sohio has worked in this area and believes that oxygen use results in a cost stand-off, excluding potential emission control advantages.

If the use of pure oxygen substantially reduces the flow of gas through the reactors, reactor design may have to be modified in order to have adequate internal heat transfer surface and at the same time maintain reactor mass flow velocity within a range necessary for proper bed expansion.

2. Effluent Neutralization

Possibly, acetic acid may be used in place of sulfuric acid for neutralizaing unconverted ammonia. The resulting ammonium acetate could be heated for ammonia recovery. Besides reducing the net ammonia consumption, this processing scheme eliminates production of unwanted by-product ammonium sulfate. A literature reference to this process modification exists.[17] However, further development work on this particular processing scheme is not justified until environmental laws discourage present neutralizer waste disposal methods.

3. Utilization of By-Products

Commercially proven processes exist for converting HCN to acrylonitrile (HCN + acetylene and HCN + ethylene oxide). Patent literature also exists for making acrylonitrile from ethylene plus HCN [11] and from acetonitrile plus formaldehyde.[12] It is possible that with process development and design work it may be found economical to incorporate one or more of these processes in the overall acrylonitrile plant as a method of eliminating net production of by-product HCN and acetonitrile. It is also possible to recycle HCN to the Sohio acrylonitrile reactors and thereby reduce if not entirely eliminate net HCN production.[16] These alternate processing schemes would not only eliminate a possible source of pollution from by-product incineration but also make better use of raw materials.

4. By-Product Incineration

There remains a question as to how much NO_x is formed in the by-product thermal incinerator. If source testing shows that substantial amounts of NO_x are formed, R & D work should be expended in order to determine optimum incinerator operating conditions for limiting NO_x emissions. This study could also be expanded to determine emissions from thermal incineration of the absorber vent stream.

5. Catalytic Incineration

It is possible that NO_x emissions from incineration of the absorber off-gas and by-products streams could be reduced by using a low temperature catalytic incinerator. The homogenous oxidation of N_2 does not occur to any extent at 1200° F. Therefore, virtually no NO_x will be made from N_2 in the feed and combustion air.

Inadequate experimental data is available on the catalytic oxidation of organic nitrogen compounds. Fuel combustion studies indicate that nitrogenous compounds are converted to NO; NO is the expected product from decomposition of ring nitrogen compounds and the rate of catalytic decomposition of NO is severely inhibited by the presence of oxygen. However, simple thermodynamic arguments predict the rate of NO formation from dissociated N and O atoms chemisorbed on the catalyst surface to be low. Consequently additional direct experimental evidence is needed to judge the NO_x yield obtained on hydrocarbon oxidation catalysts.

Textbook chemistry shows that the hydrolysis reaction

$$RCN + 2\ H_2O \longrightarrow RCOOH + NH_3$$

goes to completion on acid catalysts at 800° F. Additionally, the catalytic oxidation of NH_3 occurs readily on Pt catalysts above 520° F. Thus there are easy catalytic routes to the unwanted NO.

For the above reasons, it is doubtful that catalytic incineration would substantially reduce NO_x emissions. However, experimental data is needed on catalytic incineration of the absorber off-gas and by-product streams to prove or disprove this supposition. Since catalytic incineration has the following disadvantages,

(a) Higher operating costs than thermal incineration,

(b) Only moderate catalyst life with possible danger of catalyst fouling and poisoning.

(c) Limited oxidation activity.

any R & D work in this area should be delayed until after thermal incineration has been proved to be an inadequate control device.

XV. Research and Development Programs

The following proposed programs are for projects within the general R & D areas listed in Section XIV. These programs are limited to those R & D projects which would have a good chance of success for obtaining methods of reducing emissions from future acrylonitrile manufacture.

Project A

1. Title - Oxygen Feed plus Vent Gas Recycle for Reduced Emissions.

2. Object

To develop a modified acrylonitrile process using pure oxygen and vent gas recycle to lower gas emissions.

3. Project Cost (see Table AN-14 for cost breakdown)

Capital Expenditures		$ 125,000
Operating Costs		
Total Manpower		130,300
Services		12,100
Materials		7,500
Contingency		47,100
	Total	$ 322,000

4. Scope

On a laboratory scale, modify the Sohio acrylonitrile process by replacing part or all of the air feed with pure oxygen and by recycling absorber off-gas for dilution and improved utilization of propylene feed. Successful completion of this project could lead to a pilot plant demonstration utilizing the same pilot plant equipment employed in this study.

5. Program

(a) Engineering

Process engineering effort is required to determine if thermodynamic equilibrium favors recycle of vent gas as a method of reducing net emissions.

(b) Design Construction and Checkout

This part of the project is concerned with the design, fabrication and start-up of a laboratory scale unit. Since the Sohio acrylonitrile process uses a fluid bed reactor, a reduction in the volume of gas entering the system may have dramatic effects on conversion. For this reason, the pilot plant reactor should be designed to allow as much control as possible over temperature and residence time. In addition, multiple reactor feed inlet nozzles should be provided.

(c) Feasibility Demonstration

This part of the program calls for operation of the unit in the conventional manner; i.e. with air. This would give a base point

TABLE AN-14
DETAILED COSTS
FOR
R & D PROJECT A

ENGINEERING		
Process Design		
Process Engineer, 2 Men - 8 Weeks (each)		9,800
Contingency		1,200
		11,000
DESIGN, CONSTRUCTION & CHECKOUT		
Design Manpower: Professional - 16 Weeks		14,800
Major Equipment, Installed		125,000
Contingency		30,200
		170,000
FEASIBILITY DEMONSTRATION		
Operation		
Manpower:	Professional 4.0 Weeks	3,700
	Technician - 2 Men/Shift, 3 Shifts/Day - 6 Weeks	25,800
Services:	Analytical - 300 Hours	4,400
Materials		2,500
Contingency		4,600
		41,000
PROCESS DEVELOPMENT		
Operation		
Manpower:	Professional - 8.0 Weeks	7,400
	Technician - 2 Men/Shift, 3 Shifts/Day - 16 Weeks	68,800
Services:	Analytical - 500 Hours	7,200
	Computational	500
Materials		5,000
Contingency		11,100
		100,000

for subsequent work employing pure oxygen and recycle vent gas. Measurements would be made for the activity and selectivity of the process.

(d) Process Development

The process using oxygen would be developed with an attempt to optimize the activity and selectivity of the process. Various flow schemes could be attempted using recycled vent gases.

6. Timetable

Total time for project is estimated to be 13 months (excludes time required for delivery and construction of pilot plant equipment).

Project B

1. Title - Additional Processing of By-Products.

2. Object

To develop a modified acrylonitrile process which utilizes by-product HCN and acetonitrile from the Sohio process for additional acrylonitrile production.

3. Project Cost (see Table AN-15 for cost breakdown)

Capital Expenditures		$ 150,000
Operating Costs		
Total Manpower		76,900
Services		7,700
Materials		5,000
Contingency		80,400
	Total	$ 320,000

4. Scope

This project ranges in scope from the economic analysis of various processing schemes to the design, construction and operation of a pilot unit.

5. Program

Since technology already exists for processing HCN and acetonitrile to acrylonitrile, all that is necessary is a process engineering design study to evaluate various processing schemes. Upon completion of this engineering study, it may be necessary to construct a pilot unit to demonstrate operability and optimize operating conditions for the proposed by-product processing. If commercially proven processes are selected, pilot plant testing would not be required.

6. Timetable

Total time for project is estimated to be 16 months (excludes time required for delivery and construction of pilot plant equipment). If pilot plant work is not required project could be completed in about 6 months.

TABLE AN-15
DETAILED COSTS
FOR
R & D PROJECT B

ENGINEERING	
Process Design and Economic Evaluation	
Process Engineer, 2 men - 20 weeks (each)	24,400
Contingency	3,000
	27,400
PILOT UNIT DESIGN CONSTRUCTION & CHECKOUT	
Design Manpower: Professional - 16 weeks	14,800
Major Equipment, Installed	150,000
Contingency	70,000
	234,800
PROCESS DEVELOPMENT	
Operation	
Manpower: Professional - 12 weeks	11,100
Technician - 2 men - 26 weeks	26,600
Services: Analytical - 500 hours	7,200
Computational	500
Materials	5,000
Contingency	7,400
	57,800

Project C

1. Title - Reduction of NO_x from Combustion of By-Products.

2. Object

To outline the work required to develop a thermal combustion system to minimize NO_x emissions from the stack gases produced by combustion of hydrocarbon by-products.

3. Project Cost (see Table AN-16 for cost breakdown)

Capital Expenditures		$ 45,000
Operating Costs		
Total Manpower		40,300
Services		4,200
Materials		2,900
Contingency		10,600
	Total	$103,000

4. Scope

Existing commercial furnace operation would be considered initially. Modified system designs would be explored in order to make further significant reduction in NO_x levels. Optimum operating conditions must also be determined and the final results of this pilot investigation would be projected to a commercial scale unit.

5. Program

(a) Preliminary

(1) Equipment selection and acquisition.

Pilot unit should be able to handle 5 - 10 lbs./hr. of feed combustibles.

(2) Equipment installation and start-up.

Because of the high toxicity feed an outdoor site would be employed and the incinerator stack gas should be scrubbed.

(b) System Development

(1) Modelling

In view of the complexity of the system, a computer program model would be prepared to predict optimum operating conditions and to help point out the direction for changes in design. Kinetic and stoichiometric data would be determined primarily for the combustion of HCN and acetonitrile.

(2) Investigation of existing commercial furnace operation.

A minimum of two furnace feed compositions would be investigated : 1% and 50 wt. % acetonitrile in HCN.

(3) Investigation of new combustion systems.

An effort would be made to develop a system that would result in low NO_x emissions. A number of factors would be explored to thermally reduce NO_x emissions such as using alternate firing and quenching stages, rapid quenching, stack gas recirculation, low levels of excess air and water injection.

(4) Refinement of operation for best design.

(c) Engineering Evaluation of a Projected Commercial Installation.

6. Timetable

Total time for this program is estimated to be about 10 months (excludes time required for delivery of pilot plant equipment). It is assumed the pilot unit would be operated on a one shift per day basis.

7. Remarks

If during commercial plant source sampling or preliminary work on this R & D project it becomes apparent that NO_x production in by-product incineration is not a problem, the R & D program should be modified to include synthetic process absorber vent gas in the incinerator feed. However, if by-product nitrogen compounds form appreciable NO_x, it would be desirable to make a separate study of the process vent gas incineration. The R & D program and estimated project cost for this study would be similar to those shown for the above by-product incineration program.

TABLE AN-16
DETAILED COSTS
FOR
R & D PROJECT C

Sheet 1 of 2

INITIAL COST		
Capital Expenditure		
Equipment and Instrumentation Acquisition & Installation		45,000
Manpower		
Equipment Selection, Familiarization and Checkout		
Professional (5 weeks)		4,600
Technician (3 weeks)		1,500
Contingency		5,900
	Total	57,000
RESEARCH & DEVELOPMENT PROGRAM		
A. System Modelling		
1. Operation for Kinetic & Stoichiometric Data		
Manpower		
Professional (2 weeks)		1,800
Technician (4 weeks)		2,000
Services		
Analytical		500
Computational		200
Materials		900
2. Mathematical Modelling		
Manpower		
Professional (8 weeks)		7,400
Services		
Computational		1,500
Report		
Professional (1 week)		900
Contingency for items 1 & 2		1,800
	Total	17,000
B. System Development and Optimization		
Manpower		
Professional (12 weeks)		11,000
Technician (12 weeks)		6,100
Mechanical Craftsman (2 weeks)		700
Services		
Analytical		1,000
Computational		1,000

TABLE AN-16 CONTINUED
DETAILED COSTS
FOR
R & D PROJECT C

Sheet 2 of 2

	Materials		2,000
	Contingency		2,400
		Total	24,200
C.	Final Report		
	Professional (2 weeks)		1,800
		Total	43,000
ENGINEERING			
	Economic Evaluation		
	Manpower		
	Process Engineer (3 weeks)		1,800
	Mechanical Engineer (1 week)		700
	Contingency		500
		Total	3,000

XVI. Sampling, Monitoring and Analytical Methods for Pollutants in Air Emissions

A. Methods in Use

The principal sources of potential air contaminants from acrylonitrile production are the product absorber and by-product incinerator stacks. All plants surveyed analyzed the absorber gases at fairly frequent intervals, while two of the four have analyzed the incinerator gases at some time in the past. Depending on the recovery process, each plant has at least one flare and in some cases other minor sources of atmospheric emissions. None of the minor sources were sampled although calculated emissions were submitted in several cases.

1. Absorber Vent Gases

As may be seen in Table AN-17, the information received concerning analytical methods was not very specific. However, all four operating plants surveyed used the multi-column gas chromatograph for separation of organic constituents of the absorber vent gas, and in one case for separation of oxygen, carbon dioxide, carbon monoxide and propane. Three plants scrub the stack gases with water or hydrochloric acid to remove HCN for silver nitrate titration. One plant determines CO_2 and CO by infrared analysis.

One analytical method based on an automatic sampling and mass spectrometer analysis system was found [18]. The spectrometer output was computer analyzed to obtain a quantitative analysis of 14 compounds in a 24 minute period. The system was applied to reactor effluent gases, but probably is applicable to absorber vent gases as well. The plant using this technique has recently been closed, but the analytical procedures remain of interest.

In all cases, plant personnel expressed a high degree of confidence in the analytical results. Although specific details are lacking in the test procedures, the basic analytical principles employed are sound and the impression was gained that the methodology is highly developed. It appears that the emission data obtained should probably be regarded as sound and that independent development of sampling and analytical methods is not warranted at the present time.

2. Incineration Exhaust Gases

Only two plants performed analyses for incinerator exhaust components. Of the analytical techniques used, the EPA method 7 for NO_x and Shell Development method for SO_2 are adequately described by reference, but the others are essentially unknown. However, there appears to be no reason why EPA methods for NO_x and SO_2 could not be combined with absorber vent GC methods to obtain complete and accurate data.

B. Future Methods Development

The analytical methods available for absorber vent and incinerator exhausts are probably adequate, but vary widely from plant to plant. It would appear advantageous to obtain specific details of the techniques in use and to promote greater uniformity in the industry. An analytical package suitable for both major and minor sources at

acrylonitrile plants would probably consist of multiple column GC for the analysis of organics and combustion gases, supplemented with EPA methods for SO_2 and NO_x analysis.

TABLE AN-17
SUMMARY OF
SAMPLING AND ANALYTICAL METHODS
FOR POLLUTANTS

Sheet 1 of 2

Source	Plant	Material	Method
Absorber Vent	51-1	Various Components	Analytical methods believed to be the same as those listed for plant 51-2.
	51-2	HCN	Scrubber followed by silver nitrate titration using a modified Liebig-Deniges reaction.
		Acrylonitrile & Acetonitrile	GLC using a 2 meter x ¼" copper column containing 25 gms of 35% peg 200 on one part 80 - 100 mesh chromosorb P and 4 parts 40 - 60 mesh chromosorb P.
		O_2, CO_2, CO, C_3H_8	Double column GC with (1) 6 ft. of ¼" tubing containing 30% HMPA on 60 - 80 mesh chromosorb P, and (2) 12 ft. of ¼" tubing containing 13x molecular sieve plus 60 - 80 mesh column packing.
	51-3	Acrylonitrile	Water scrubber-analysis unknown.
		CH_4, C_2H_6, C_2H_4, C_2H_8, C_2H_6	Flame ionization GC using one column containing Perkin Elmer type S sorbent.
		CO, CO_2	Infrared.
	51-4	HCN, NH_3	Hydrochloric acid scrubber. Titrate NH_3 with 0.3 N sodium hydroxide. Titrate HCN with 0.001 N silver nitrate.
		Organics	Double column GC.
Incinerator Exhaust	51-1	HCN, NH_3	Draeger tubes.
		NO_x	EPA method 7.[20]
	51-2	O_2, CO_2, CO, N_2	See plant 51-2 absorber vent.
		NO_x	Measured, but method unknown.
		SO_2	Shell method.[19]

TABLE AN-17 CONTINUED
SUMMARY OF
SAMPLINC AND ANALYTICAL METHODS
FOR POLLUTANTS

Sheet 2 of 2

Source	Plant	Material	Method
Incinerator Exhaust	51-2	Organics	Method unknown.
	51-3	None	
	51-4	None	

XVII. Emergency Action Plan (EAP) For Air Pollution Episodes

A. Types of Episodes

The alleviation of Air Pollution Episodes as suggested by the U.S. Environmental Protection Agency is based on a pre-planned episode emission reduction scheme. The criteria that set this scheme into motion are:

1. Alert Status - The alert level is that concentration of pollutants at which short-term health effects can be expected to occur.

2. Warning Status - The warning level indicates that air quality is continuing to deteriorate and that additional abatement actions are necessary.

3. Emergency Status - The emergency level is that level at which a substantial endangerment to human health can be expected. These criteria are absolute in the sense that they represent a level of pollution that must not be allowed to occur.

B. Sources of Emission

As outlined in the foregoing in-depth study of acrylonitrile manufacture, there are usually four continuous and two intermittent vent streams to the atmosphere.

1. Continuous Streams

   (a) Absorber Vent Gas - This stream represents the primary potential air emission in the Sohio acrylonitrile process and consists of the gross reactor effluent after neutralization and recovery of nitriles and HCN. Under normal conditions, the quantity of absorber vent hydrocarbon emissions (excluding propane and propylene) are primarily influenced by the amount of air charged to the reactors. Air rates are usually held constant to maintain catalyst fluidization. Several plants currently have plans to install an incinerator or catalytic device to control emissions in this vent stream. Where this is done, it should in most cases diminish the need to take emergency action during air pollution episodes.

   (b) Product Fractionation Vent - This vent represents a combination of several small streams, which vary greatly in composition depending upon type of fractionation system used for product recovery. This material is usually sent to an incinerator or flare which reduces organic emissions.

   (c) Product Storage Vent - The product storage atmospheric vent is small due to the low vapor pressure of acrylonitrile and acetonitrile. Vent material from HCN storage is burned for control of organic emissions.

   (d) By Product Incineration - The second most voluminous air emission is represneted by the by-product incinerator flue gas. The normal emissions are the products of combustion

plus small amounts of NOx derived from burning organics having nitrogen in their structure. The flow characteristics are in some instances intermittent as indicated in Table AN-3A. Presently, portions of the unwanted waste by-products are diverted to deep well disposal.

2. Intermittent Air Emissions

(a) Process Vent Gas - During reactor start-up, the reactor effluent stream exhausts directly to the atmosphere. This occurs during heat up, the ammonia burn phase and for a short period following the introduction of proyplene into the reactor. The heat up is accomplished by heating air with natural gas and consequently, the only emissions during this period are the products of combustion. Following the introduction of ammonia, the oxygen content of the reactor effluent is allowed to drop to a low level before propylene is admitted. During the ammonia burn phase, most of the ammonia reacts with oxygen to form nitrogen and water vapor. After introducing propylene feed, the reactor effluent stream is routed into the neutralizer and absorber system. Reportedly, the complete reactor start-up sequence is completed in about one hour. However, the most significant contaminants emitted during this period are propylene and acrylonitrile which are emitted for periods of five to 20 minutes before the reactor effluent is routed to the quench and recovery system.

This start-up procedure is applicable whether for one reactor of a battery, with the other reactors operating, or for the start-up of all reactors in a multi reactor plant. However, the usual practice in the latter instance is to place only one reactor into service, at any one time.

(b) Emergency Relief - During plant up-set or other emergencies, the following streams are controlled by routing them to the flare or by-product incinerator:

(1) Propylene Sotrage - Relief valves in this service are routed to the flare.

(2) Propylene Feed - This is vented to the flare if the source of heat for vaporization is lost and the vaporizer freezes up. In addition, propylene vaporizers are vented to the flare during scheduled plant shutdowns.

(3) By-Product HCN - This is usually sent to an incinerator unless it is marketed. An upset in the fractionation systems could result in it being diverted to incineration.

C. Abatement Techniques

As the various levels of the pre-planned episode emission reduction scheme are declared (Alert, Warning and Emergency) a progressive reduction in the amount of air pollutants must be made. This could ultimately lead to total curtailment of pollutant emissions if the emergency level becomes imminent. The extent of required cutback in emissions from acrylonitrile

plants will depend on the relative amount of offending constituents contributed by acrylonitrile production to the overall emissions which resulted in the pollution episode. This plus other factors will be used by control authorities in determining the amount of emissions to be tolerated during various episodes. The degree of emission curtailment should recognize plant size and location and should also be dependent upon the extent of air contaminant emission controls employed by the specific plants.

To obtain a partial reduction inair pollutant emissions, several options are available to the acrylonitrile plant operator. Acrylonitrile manufacturing facilities generally consist of single or multiple reactor systems, with each system or plant containing separate product recovery equipment. A multiple reactor system provides for increased flexibility to affect a partial reduction in air pollutant emissions during an air pollution alert. This is possible since individual reactors can be removed from service resulting in a reduction of total absorber vent gas emissions. The reactors removed from service can either be maintained in standby condition (by holding reactor temperature at 800° F) or taken off line and allowed to cool.

If a single reactor system must be taken off line and cooled to near ambient conditions, it will require a minimum of 24 hours to heat up the system and conduct a normal start-up. Time requirements for start-up of single reactor systems and multiple reactor systems vary depending on the availability of utilities (steam).

Problems which could arise in the event an episode might dictate a complete shutdown in winter during sub-freezing temperatures. The acrylonitrile plant uses large amounts of water circulation for product recovery. If these circulation systems or the steam generation system freeze, a start-up might require weeks.

A single reactor system can be taken out of service in two-three hours if it is maintained in standby condition. To resume production from this point would normally require two to four hours. A reactor start-up requires additional utilities and personnel. The availability of these might increase the time requirement by up to six hours.

Reactor "turndown" or reduction in reactant feed will proportionally reduce the emission of unreacted hydrocarbons and carbon oxides in the absorber vent gas. Emission to the atmosphere of the desired reaction products would also normally be reduced. The latter reduction will be a function of throughput and efficiency of the absorber system. Absorber efficiency is dependent onlow temperature operation. The absorber system is subject to fouling by polymers and tars. Therefore, periodic cleaning of exchange surfaces is required to maintain good heat transfer and efficient operation. It has been reported by plant 51-2 that a turndown to 60 percent of maximum rate is possible. In an emergency, this turndown can be accomplished in one hour.

It should be noted that reactor turndown will proportionally decrease steam production. This reduction may adversely influence the operation of other process units which depend on this source of steam. This would require adjustments in the steam system which might require shutdown or curtail operation of units not directly related to the pollution episode.

1. Declaration of Alert Condition - When an alert condition is declared the episode emission reduction plan is immediately set into motion. Under this plan, in addition to notifying the manufacturer of the alert condition, it may be deemed necessary to reduce emissions from acrylonitrile manufacture somewhat to conform in the overall reduction plan set forth by the Environmental Protection authorities. This can be accomplished by a reduction in acrylonitrile production which will reduce the principal source of emissions represented by the absorber vent.

   During an alert condition it should be possible to reduce emissions resulting from by-product incineration. Production of by-products would be reduced if a cutback is made in acrylonitrile production. In some plants, by-products are presently burned on an intermittent basis. In these and other plants it should be possible to curtail this incineration during an episode provided adequate by-products storage facilities or an alternative method of disposal (deep well injection) is available. The other sources of atmospheric emissions (product fractionation vent and product storage vent) are more difficult to control and, since they are minor quantities, no attempt other than employing maximum cooling of tower overhead streams is suggested for their reduction. The time required to effect reductions will be from one to three hours. Usually the alert condition can be expected to continue for 12 hours or more.

2. Declaration of Warning Condition - If an air pollution warning episode is announced, a substantial reduction of air contaminants is desirable even to the point of assuming reasonable economic hardships in the cutback of production and allied operations. This could involve a 50 to 60 percent decrease in acrylonitrile production which would reduce the principal source of emission represented by the absorber vent gas by a value approximately equivalent to the reduction made in plant capacity. The emissions from the product fractionation and stroage vents may decrease to some degree by virtue of reduced acrylonitrile production.

3. Emergency Condition - When it appears that an air pollution emergency is imminent, all air contaminants may have to be eliminated by ceasing or curtailing production and allied operations to the extent possible without causing injury to persons or damage to equipment.

   The cessation of reactor operation whether wholly or in part will not result in increased emissions. On the other hand, during the subsequent plant start-up, there is an increase in atmospheric emissions for one hour or less. This results from the requirement of direct atmospheric venting of reactors during start-up. On the average, hydrocarbon emissions during this period will be three to seven times the normal on-stream value. This hydrocarbon, which is primarily acrylonitrile, represents about 10 wt. percent of the total vent stream. Because of the large quantity of combustibles and variation in composition, it is unlikely that all of this stream could be sent to the by-product or absorber vent gas incinerators wihtout posing temperature control problems.

Therefore, in most instances, the partial reduction in air emissions during an alert episode may best be accomplished by a turndown in plant capacity. It should be noted that in plants that incorporate absorber vent gas incineration with steam generation, it may be necessary to use additional supplemental fuel during plant turndown operation in order to produce sufficient steam for other process units which are dependent on this steam generator.

D. Economic Considerations

The economic impact on the manufacturer of curtailing operations during any of the air pollution episodes is based on the duration and number of episodes in a given period. It is indicated that the normal duration of air pollution episodes that occur in various areas of Eastern U.S. is usually from one to seven days with meteorology episode potentials as high as 80 per year.[22] The frequency of air pollution episodes in any given area is indicated as being one to four per year. These data do not differentiate between the episode levels set forth in the early paragraphs of this section. Normally since the alert level does not require a cutback in production, it will not influence plant economics. Therefore, in discussing economic considerations resulting from the air pollution abatement plan, it is only necessary to estimate the frequency and number of warning and emergency episodes. For the economic study, it has been assumed that three warning and no emergency episodes occur per year. Each warning episode is assumed to require a 50 percent reduction in air contaminants for a period of five and one half days. This then equates to a complete loss in plant production for about eight and one half days per year.

The relative finanaical impact resulting from this loss in production is shown in Table AN-18. This table contains comparative manufacturing costs for an existing 200 MM lbs./year facility without extensive pollution control (Table AN-10) and for a most feasible new facility of the same capacity (Table AN-11). Economics are shown for each of these plants with and without the financial impact accredited to the air pollution episodes. It should be noted that whereas the assumed cutback in acrylonitrile production for emission control appears small (2.5 percent on a yearly basis), it reduces net profit by about seven percent.

E. Summary of Estimated Emissions

In the foregoing a reduction in air pollutant emissions was suggested for the various air pollution levels that may be encountered. This was predicated on existing plants which do not employ combustion devices on the absorber vent stream. Special consideration should be made in the EAP for Air Pollution Episode Avoidance for new and existing plants that do employ this incineration.

The following tabulation presents estimated air emissions for a typical present-day system without incineration and the most feasible new plant with this type of control.

Pollutant	Typical Present System Average Emissions, Tons/Ton	Most Feasible New Plant Average Emissions, Tons/Ton
Hydrocarbon	0.1071	0.0005
NOx	0.0067	0.0098
CO	0.1222	---
Total Emissions	0.2360	0.0103

As noted in the above, total emissions for the most feasible new plant has been reduced to less than five percent of that estimated for the typical present system without absorber vent gas incineration. However, emissions of NOx would increase by about 50 percent over that projected for the plant not employing an incinerator.

The particular type and concentration of pollutants in the atmosphere at the time of the episode would dictate the degree to which a reduction would be made on the most feasible new plant. If NOx is the offending material, then a reduction in plant production should be made as outlined under "Declaration of Warning Condition". In this case NOx emissions would be reduced in proportion to the reduction of acrylonitrile production.

If the alert is called on the basis of excess hydrocarbons or CO concentration in the ambient air, less severe cutbacks in production need to be taken. This is especially true if incinerators are employed for pollution control.

The primary contaminants emitted from this process are hydrocarbons, CO and to a lesser extent, NOx. Therefore, if an alert is called on the basis of SO_2 or particulates, curtailing the acrylonitrile operation should not be necessary.

TABLE AN-18

FINANCIAL IMPACT OF AIR POLLUTION EPISODES

ON MANUFACTURING COSTS (a)

FOR 200 MM LBS./YEAR ACRYLONITRILE MANUFACTURING FACILITY

(No Credit For By-Products)

Type of Operation	TYPICAL EXISTING PLANT		MOST FEASIBLE NEW PLANT (b)	
	No Cutback In Production (Table AN-10)	Assuming 8.5 Days Lost Production	No Cutback In Production (Table AN-11)	Assuming 8.5 Days Lost Production
Direct Manufacturing Cost, $/Yr.				
Raw Materials				
90% Propylene @ 2.8¢/Lb.	7,980,000	7,781,000	7,980,000	7,781,000
Ammonia @ 1.5¢/Lb.	1,480,000	1,443,000	1,480,000	1,443,000
Sulfuric Acid @ 1.5¢/Lb.	120,000	117,000	120,000	117,000
Catalyst and Chemicals	1,000,000	988,000	1,000,000	988,000
Labor	340,000	340,000	360,000	360,000
Maintenance	1,200,000	1,200,000	1,220,000	1,220,000
Utilities	1,800,000	1,755,000	1,760,000	1,716,000
	13,920,000	13,624,000	13,920,000	13,625,000
Indirect Manufacturing Cost, $/Yr.				
Plant Overhead	380,000	380,000	380,000	380,000
Fixed Manufacturing Cost, $/Yr.				
Depreciation, Insurance and Property Tax	2,960,000	2,960,000	3,040,000	3,040,000

TABLE AN-18

CONTINUED - PAGE 2

Type of Operation	TYPICAL EXISTING PLANT		MOST FEASIBLE NEW PLANT (b)	
	No Cutback In Production (Table AN-10)	Assuming 8.5 Days Lost Production	No Cutback In Production (Table AN-11)	Assuming 8.5 Days Lost Production
Total Manufacturing Cost, $/Yr.	17,260,000	16,964,000	17,340,000	17,045,000
General Expenses, $/Yr.				
Administration, Sales, Research and Financial	2,480,000	2,480,000	2,520,000	2,520,000
Total Cost, $/Yr.				
Selling Price (Acrylonitrile @ 12¢/Lb.)	24,000,000	23,400,000	24,000,000	23,400,000
Profit Before Taxes	4,260,000	3,956,000	4,140,000	3,835,000
Profit After 52% Tax	2,045,000	1,899,000	1,987,000	1,841,000
Cash Flow	4,445,000	4,299,000	4,463,000	4,317,000
ROI (NPAT X 100/Investment)	8.52%	7.91%	8.03%	7.44%

(a) Designed to show only relative effect.

(b) Includes a thermal incinerator plus waste heat boiler on the absorber vent stream.

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APPENDIX I

BASIS OF THE STUDY

I. Industry Survey

The study which led to this document was undertaken to obtain information about selected production processes that are practiced in the Petrochemical Industry. The objective of the study was to provide data for the EPA to use in the fulfillment of their obligations under the Clean Air Amendments of 1970.

The information obtained during the study includes industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions and descriptions of emission control devices currently in use. The principal source for these data was an Industry Questionnaire but it was supplemented by plant visits, literature searches, in-house background knowledge and direct support from the Manufacturing Chemists Association.

More than 200 petrochemicals are currently produced in the United States, and many of these by two or more different processes. It was obvious that the most immediate need was to study the largest tonnage, fastest growth processes that produce the most pollution. Consequently, the following 32 chemicals (as produced by a total of 41 different processes) were selected for study:

Acetaldehyde (two processes)
Acetic Acid (three processes)
Acetic Anhydride
Acrylonitrile
Adipic Acid
Adiponitrile (two processes)
Carbon Black
Carbon Disulfide
Cyclohexanone
Ethylene
Ethylene Dichloride (two processes)
Ethylene Oxide (two processes)
Formaldehyde (two processes)
Glycerol
Hydrogen Cyanide
Maleic Anhydride
Nylon 6
Nylon 6,6
"Oxo" Alcohols and Aldehydes
Phenol
Phthalic Anhydride (two processes)
Polyethylene (high density)
Polyethylene (low density)
Polypropylene
Polystyrene
Polyvinyl Chloride
Styrene
Styrene - Butadiene Rubber
Terephthalic Acid (1)
Toluene Di-isocyanate (2)
Vinyl Acetate (two processes)
Vinyl Chloride

(1) Includes dimethyl terephthalate.
(2) Includes methylenediphenyl and polymethylene polyphenyl isocyanates.

The Industry Questionnaire, which was used as the main source of information, was the result of cooperative efforts between the EPA, Air Products and the EPA's Industry Advisory Committee. After receiving approval from the Office of Management and Budget, the questionnaire was sent to selected producers of most of the chemicals listed above. The data obtained from the returned questionnaires formed the basis for what have been named "Survey Reports". These have been separately published in four volumes, numbered EPA-450/3-73-005a, b, c, and d and entitled "Survey Reports on Atmospheric Emissions from the Petrochemical Industry - Volumes I, II, III, and IV.

The purpose of the survey reports was to screen the various petrochemical processes into the "more" and "less - significantly polluting processes". Obviously, significance of pollution is a term which is difficult if not impossible to define because value judgements are involved. Recognizing this difficulty, a quantitative method for Significant Emission Index (SEI) was developed. This procedure is discussed and illustrated in Appendix II of this report. Each survey report includes the calculation of an SEI for the petrochemical that is the subject of the report. These SEI's have been incorporated into the Emission Summary Table that constitutes part of this Appendix (Table I). This table can be used as an aid when establishing priorities in the work required to set standards for emission controls on new stationary sources of air pollution in accordance with the terms of the Clean Air Amendments of 1970.

The completed survey reports constitute a preliminary data bank on each of the processes studied. In addition to the SEI calculation, each report includes a general introductory discussion of the process, a process description (including chemical reactions), a simplified process flow diagram, as well as heat and material balances. More pertinent to the air pollution study, each report lists and discusses the sources of air emissions (including odors and fugitive emissions) and the types of air pollution control equipment employed. In tabular form, each reports summarizes the emission data (amount, composition, temperature, and frequency); the sampling and analytical techniques; stack numbers and dimensions; and emission control device data (types, sizes, capital and operating costs, and efficiencies).

Calculation of efficiency on a pollution control device is not necessarily a simple and straight-forward procedure. Consequently, two rating techniques were developed for each type of device, as follows:

1. For flares, incinerators, and boilers a Completeness of Combustion Rating (CCR) and Significance of Emission Reduction Rating (SERR) were used.

2. For scrubbers and dust removal equipment, a Specific Pollutant Efficiency (SE) and a SERR were used.

The bases for these ratings and example calculations are included in Appendix III of this report.

II. In-Depth Studies

The original performance concept was to select a number of petrochemical processes as "significant polluters", on the basis of data contained in completed questionnaires. These processes were then to be studied "in-depth". However, the overall time schedule was such that the EPA requested an initial selection of three processes on the basis that they would probably turn out to be "significant polluters". The processes selected in this manner were:

1. The Furnace Process for producing Carbon Black.

2. The Sohio Process for producing Acrylonitrile.

3. The Oxychlorination Process for producing 1,2 Dichloroethane (Ethylene Dichloride) from Ethylene.

TABLE 1
EMISSIONS SUMMARY

	ESTIMATED (1) CURRENT AIR EMISSIONS, MM LBS./YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5)
Acetaldehyde via Ethylene	1.1	0	0	0	0	1.1	86
via Ethanol	0	0	0	0	27	27	27
Acetic Acid via Methanol	0	0	0.01	0	0	0.01	1
via Butane	40	0	0.04	0	14	54	3,215
via Acetaldehyde	6.1	0	0	0	1.3	7.4	490
Acetic Anhydride via Acetic Acid	3.1	0	0	0	5.5	8.6	253
Acrylonitrile (9)	183	0	5.5	0	196	385	15,000
Adipic Acid	0	0.2	29.6	0	0.14	30	1,190
Adiponitrile via Butadiene	11.2	4.7	50.5	0	0	66.4	3,200
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	156	8.1	6.9	21.6	3,870	4,060	17,544
Carbon Disulfide	0.15	0.3	0.1	4.5	0	5	120
Cyclohexanone	70	0	0	0	77.5	148	5,700
Dimethyl Terephthalate (+TPA)	91	1.4	0.1	1.0	53	146.5	7,460
Ethylene	15	0.2	0.2	2.0	0.2	17.6	1,240
Ethylene Dichloride via Oxychlorination	95.1	0.4	0	0	21.8	117.3	7,650
via Direct Chlorination	29	0	0	0	0	29	2,300
Ethylene Oxide	85.8	0	0.3	0.1	0	86.2	6,880
Formaldehyde via Silver Catalyst	23.8	0	0	0	107.2	131	1,955
via Iron Oxide Catalyst	25.7	0	0	0	24.9	50.6	2,070
Glycerol via Epichlorohydrin	16	0	0	0	0	16	1,280
Hydrogen Cyanide Direct Process	0.5	0	0.41	0	0	0.91	56
Isocysnates	1.3	0.8	0	0.02	86	88	231
Maleic Anhydride	34	0	0	0	260	294	2,950
Nylon 6	0	1.5	0	0	0	1.5	90
Nylon 6,6	0	5.5	0	0	0	5.5	330
Oxo Process	5.25	0.01	0.07	0	19.5	24.8	440
Phenol	24.3	0	0	0	0	24.3	1,940
Phthalic Anhydride via O-Xylene	0.1	5.1	0.3	2.6	43.6	51.7	422
via Naphthalene	0	1.9	0	0	45	47	160
High Density Polyethylene	79	2.3	0	0	0	81.3	6,400
Low Density Polyethylene	75	1.4	0	0	0	76.4	6,100
Polypropylene	37.5	0.1	0	0	0	37.6	2,950
Polystyrene	20	0.4	0	1.2	0	21.6	1,650
Polyvinyl Chloride	62	12	0	0	0	74	5,700
Styrene	4.3	0.07	0.14	0	0	4.5	355
Styrene-Butadiene Rubber	9.4	1.6	0	0.9	0	12	870
Vinyl Acetate via Acetylene	5.3	0	0	0	0	5.3	425
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	17.6	0.6	0	0	0	18.2	1,460
Totals	1,227.6	49.1	94.2	33.9	4,852.6	6,225.9 (7)	110,220 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) Emissions based on what is now an obsolete catalyst. See Report No. EPA-450/3-73-006 b for up-to-date information.

TABLE I
EMISSION SUMMARY

	ESTIMATED ADDITIONAL (2) AIR EMISSIONS IN 1980, MM LBS./YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5,6)
Acetaldehyde via Ethylene	1.2	0	0	0	0	1.2	96
via Ethanol	0	0	0	0	0	0	0
Acetic Acid via Methanol	0	0	0.04	0	0	0.04	2
via Butane	0	0	0	0	0	0	0
via Acetaldehyde	12.2	0	0	0	2.5	14.7	980
Acetic Anhydride via Acetic Acid	0.73	0	0	0	1.42	2.15	60
Acrylonitrile (9)	284	0	8.5	0	304	596	23,000
Adipic Acid	0	0.14	19.3	0	0.09	19.5	779
Adiponitrile via Butadiene	10.5	4.4	47.5	0	0	62.4	3,010
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	64	3.3	2.8	8.9	1,590	1,670	7,200
Carbon Disulfide	0.04	0.07	0.03	1.1	0	1.24	30
Cyclohexanone	77.2	0	0	0	85.1	162	6,260
Dimethyl Terephthalate (+TPA)	73.8	1.1	0.07	0.84	42.9	118.7	6,040
Ethylene	14.8	0.2	0.2	61.5	0.2	77	2,430
Ethylene Dichloride via Oxychlorination	110	0.5	0	0	25	136	8,800
via Direct Chlorination	34.2	0	0	0	0	34.2	2,740
Ethylene Oxide	32.8	0	0.15	0.05	0	33	2,650
Formaldehyde via Silver Catalyst	14.8	0	0	0	66.7	81.5	1,250
via Iron Oxide Catalyst	17.6	0	0	0	17.0	34.6	1,445
Glycerol via Epichlorohydrin	8.9	0	0	0	0	8.9	700
Hydrogen Cyanide Direct Process	0	0	0	0	0	0	0
Isocyanates	1.2	0.7	0	0.02	85	87	225
Maleic Anhydride	31	0	0	0	241	272	2,720
Nylon 6	0	3.2	0	0	0	3.2	194
Nylon 6,6	0	5.3	0	0	0	5.3	318
Oxo Process	3.86	0.01	0.05	0	14.3	18.2	325
Phenol	21.3	0	0	0	0	21.3	1,704
Phthalic Anhydride via O-Xylene	0.3	13.2	0.8	6.8	113	134	1,100
via Naphthalene	0	0	0	0	0	0	0
High Density Polyethylene	210	6.2	0	0	0	216	17,200
Low Density Polyethylene	262	5	0	0	0	267	21,300
Polypropylene	152	0.5	0	0	0	152.5	12,190
Polystyrene	20	0.34	0	1.13	0	21.47	1,640
Polyvinyl Chloride	53	10	0	0	0	63	4,840
Styrene	3.1	0.05	0.1	0	0	3.25	225
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	2.34	170
Vinyl Acetate via Acetylene	4.5	0	0	0	0	4.5	360
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	26.3	0.9	0	0	0	27.2	2,170
Totals	1,547.2	55.9	79.5	80.5	2,588	4,351.9	134,213 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 40, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down duw to rounding.
(9) See sheet 1 of 3.

TABLE I
EMISSIONS SUMMARY

	Emissions (2), MM Lbs./Year		Estimated Number of New Plants (1973 - 1980)	Total Estimated Capacity MM Lbs./Year	
	Total by 1980	Total Weighted (5) by 1980		Current	By 1980
Acetaldehyde via Ethylene	2.3	182	6	1,160	2,460
via Ethanol	27	27	0	966	966
Acetic Acid via Methanol	0.05	3	4	400	1,800
via Butane	54	3,215	0	1,020	500
via Acetaldehyde	22	1,470	3	875	2,015
Acetic Anhydride via Acetic Acid	10.8	313	3	1,705	2,100
Acrylonitrile (9)	980	38,000	5	1,165	3,700 (8)
Adipic Acid	50	1,970	7	1,430	2,200
Adiponitrile via Butadiene	128.8	6,210	4	435	845
via Adipic Acid	1.1	60	3	280	550
Carbon Black	5,730	24,740	13	3,000	5,000 (8)
Carbon Disulfide	6.3	150	2	871	1,100
Cyclohexanone	310	11,960	10	1,800	5,600
Dimethyl Terephthalate (+TPA)	265	13,500	8	2,865	5,900
Ethylene	94	3,670	21	22,295	40,000
Ethylene Dichloride via Oxychlorination	253	16,450	8	4,450	8,250 (8)
via Direct Chlorination	63	5,040	10	5,593	11,540
Ethylene Oxide	120	9,530	15	4,191	6,800 (8)
Formaldehyde via Silver Catalyst	212.5	3,205	40	5,914	9,000
via Iron Oxide Catalyst	85	3,515	12	1,729	3,520 (8)
Glycerol via Epichlorohydrin	25	2,000	1	245	380
Hydrogen Cyanide Direct Process	0.5 (10)	28 (10)	0	412	202
Isocyanates	175	456	10	1,088	2,120
Maleic Anhydride	566	5,670	6	359	720
Nylon 6	4.7	284	10	486	1,500
Nylon 6,6	10.8	650	10	1,523	3,000
Oxo Process	43	765	6	1,727	3,000
Phenol	46	3,640	11	2,363	4,200
Phthalic Anhydride via O-Xylene	186	1,522	6	720	1,800 (8)
via Naphthalene	47	160	0	603	528
High Density Polyethylene	297	23,600	31	2,315	8,500
Low Density Polyethylene	343	27,400	41	5,269	21,100
Polypropylene	190	15,140	32	1,160	5,800
Polystyrene	43	3,290	23	3,500	6,700
Polyvinyl Chloride	137	10,540	25	4,375	8,000
Styrene	7.4	610	9	5,953	10,000
Styrene-Butadiene Rubber	14	1,040	4	4,464	5,230
Vinyl Acetate via Acetylene	9.8	785	1	206	356
via Ethylene	TR	TR	4	1,280	2,200
Vinyl Chloride	45	3,630	10	5,400	13,000
Totals	10,605 (7)	244,420 (7)			

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(8) By 1985.
(9) See sheet 1 of 3
(10) Due to anticipated future shut down of marginal plants.

In order to obtain data on these processes, the operators and/or licensors of each were approached directly by Air Products' personnel. This, of course, was a slow and tedious method of data collection because mass mailing techniques could not be used, nor could the request for data be identified as an "Official EPA Requirement". Yet, by the time that OMB approval was given for use of the Industry Questionnaire, a substantial volume of data pertaining to each process had already been received. The value of this procedure is indicated by the fact that first drafts of these three reports had already been submitted to the EPA, and reviewed by the Industry Advisory Committee, prior to the completion of many of the survey reports.

In addition, because of timing requirements, the EPA decided that three additional chemicals be "nominated" for in-depth study. These were phthalic anhydride, formaldehyde and ethylene oxide. Consequently, four additional in-depth studies were undertaken, as follows:

1. Air Oxidation of Ortho-Xylene to produce Phthalic Anhydride.

2. Air Oxidation of Methanol in a Methanol Rich Process to produce Formaldehyde over a Silver Catalyst. (Also, the subject of a survey report.)

3. Air Oxidation of Methanol in a Methanol-Lean Process to produce Formaldehyde over an Iron Oxide Catalyst.

4. Direct Oxidation of Ethylene to produce Ethylene Oxide.

The primary data source for these was the Industry Questionnaire, although SEI rankings had not been completed by the time the choices were made.

The Survey Reports, having now been completed are available, for use in the selection of additional processes for in-depth study.

INTRODUCTION TO APPENDIX II AND III

The following discussions describe techniques that were developed for the single purpose of providing a portion of the guidance required in the selection of processes for in-depth study. It is believed that the underlying concepts of these techniques are sound. However, use of them without substantial further refinement is discouraged because the data base for their specifics is not sufficiently accurate for wide application. The subjects covered in the Appendix II discussion are:

1. Prediction of numbers of new plants.

2. Prediction of emissions from the new plants on a weighted (significance) basis.

The subject covered in the Appendix III discussion is:

Calculation of pollution control device efficiency on a variety of bases, including a weighted (significance) basis.

It should be noted that the weighting factors used are arbitrary. Hence, if any reader of this report wishes to determine the effect of different weighing factors, the calculation technique permits changes in these, at the reader's discretion.

APPENDIX II

Number of New Plants*

Attached Table 1 illustrates the format for this calculation. Briefly, the procedure is as follows:

1. For each petrochemical that is to be evaluated, estimate what amount of today's production capacity is likely to be on-stream in 1980. This will be done by subtracting plants having marginal economics due either to their size or to the employment of an out-of-date process.

2. Estimate the 1980 demand for the chemical and assume a 1980 installed capacity that will be required in order to satisfy this demand.

3. Estimate the portion of the excess of the 1980 required capacity over today's remaining capacity that will be made up by installation of each process that is being evaluated.

4. Estimate an economic plant or unit size on the basis of today's technology.

5. Divide the total required new capacity for each process by the economic plant size to obtain the number of new units.

In order to illustrate the procedure, data have been incorporated into Table I, for the three processes for producing carbon black, namely the furnace process, the relatively non-polluting thermal process, and the non-growth channel process.

*The format is based on 1980, but any future year may be selected.

Table 1. Number of New Plants by 1980

Chemical	Process	Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
Carbon Black	Furnace	4,000	0	4,000	4,500	5,000	1,000	90	11 - 12
	Channel	100	0	100	100	100	0	30	0
	Thermal	200	0	200	400	500	300	150	2

Notes: 1. Capacity units all in MM lbs./year.

2. 1980 demand based on studies prepared for EPA by Processes Research, Inc. and MSA Research Corporation.

Increased Emissions (Weighted) by 1980

Attached Table 2 illustrates the format for this calculation. However, more important than format is a proposal for a weighting basis. There is a wide divergence of opinion on which pollutants are more noxious and even when agreement can be reached on an order of noxiousness, disagreements remain as to relative magnitudes for tolerance factors. In general pollutants from the petrochemical industry can be broken down into categories of hydrogen sulfide, hydrocarbons, particulates, carbon monoxide, and oxides of sulfur and nitrogen. Of course, two of these can be further broken down; hydrocarbons into paraffins, olefins, chlorinated hydrocarbons, nitrogen or sulfur bearing hydrocarbons, etc. and particulates into ash, catalyst, finely divided end products, etc. It was felt that no useful end is served by creating a large number of sub-groupings because it would merely compound the problem of assigning a weighting factor. Therefore, it was proposed to classify all pollutants into one of five of the six categories with hydrogen sulfide included with hydrocarbons.

There appears to be general agreement among the experts that carbon monoxide is the least noxious of the five and that NO_x is somewhat more noxious than SO_x. However, there are widely divergent opinions concerning hydrocarbons and particulates - probably due to the fact that these are both widely divergent categories. In recent years, at least two authors have attempted to assign tolerance factors to these five categories. Babcock (1), based his on the proposed 1969 California standards for one hour ambient air conditions with his own standard used for hydrocarbons.

On the other hand, Walther (2), based his ranking on both primary and secondary standards for a 24-hour period. Both authors found it necessary to extrapolate some of the basic standards to the chosen time period. Their rankings, on an effect factor basis with carbon monoxide arbitrarily used as a reference are as follows:

	Babcock	Walther	
		Primary	Secondary
Hydrocarbons	2.1	125	125
Particulates	107	21.5	37.3
NO_x	77.9	22.4	22.4
SO_x	28.1	15.3	21.5
CO	1	1	1

Recognizing that it is completely unscientific and potentially subject to substantial criticism it was proposed to take arithmetic averages of the above values and round them to the nearest multiple of ten to establish a rating basis as follows:

	Average	Rounded
Hydrocarbons	84.0	80
Particulates	55.3	60
NO_x	40.9	40
SO_x	21.6	20
CO	1	1

Table 2. Weighted Emission Rates

Chemical_____

Process_____

Increased Capacity_____

Pollutant	Emissions, Lbs./Lb.	Increased Emissions Lbs./Year	Weighting Factors	Weighted Emissions Lbs./Year
Hydrocarbons			80	
Particulates			60	
NO_x			40	
SO_x			20	
CO			1	
			Total	

Increased Emissions (Weighted) by 1980 (continued)

This ranking can be defended qualitatively, if not quantitatively for the following reasons:

1. The level of noxiousness follows the same sequence as is obtained using national air quality standards.

2. Approximately two orders of magnitude exist between top and bottom rankings.

3. Hydrocarbons should probably have a lower value than in the Walther analysis because such relatively non-noxious compounds as ethane and propane are included.

4. Hydrocarbons should probably have a higher value than in the Babcock analysis because such noxious (or posionous) substances as aromatics, chlorinated hydrocarbons, phenol, formaldehyde, and cyanides are included.

5. Particulates should probably have a higher value than in the Walther analysis because national air standards are based mostly on fly ash while emissions from the petrochemical industry are more noxious being such things as carbon black, phthalic anhydride, PVC dust, active catalysts, etc.

6. NO_x should probably have a higher value than in the Walther analysis because its role in oxidant synthesis has been neglected. This is demonstrated in Babcock's analysis.

Briefly, the procedure, using the recommended factors and Table 2, is as follows:

1. Determine the emission rate for each major pollutant category in terms of pounds of pollutant per pound of final product. (This determination was made on the basis of data reported on returned questionnaires in the Survey Reports).

2. Multiply these emission rates by the estimate of increased production capacity to be installed by 1980 (as calculated while determining the number of new plants), to determine the estimated pounds of new emissions of each pollutant.

3. Multiply the pounds of new emissions of each pollutant by its weighting factor to determine a weighted pounds of new emissions for each pollutant.

4. Total the weighted pounds of new emissions for all pollutants to obtain an estimate of the significance of emission from the process being evaluated. It was proposed that this total be named "Significant Emission Index" and abbreviated "SEI".

It should be pointed out that the concepts outlined above are not completely original and considerable credit should be given to Mr. L. B. Evans of the EPA for setting up the formats of these evaluating procedures.

Increased Emissions (Weighted) by 1980 (continued)

(1) Babcock, L. F., "A Combined Pollution Index for Measurement of Total Air Pollution," JAPCA, October, 1970; Vol. 20, No. 10; pp 653-659

(2) Walther, E. G., "A Rating of the Major Air Pollutants and Their Sources by Effect", JAPCA, May, 1972; Vol. 22, No. 5; pp 352-355

Appendix III
Efficiency of Pollution Control Devices

Incinerators and Flares

The burning process is unique among the various techniques for reducing air pollution in that it does not remove the noxious substance but changes it to a different and hopefully less noxious form. It can be, and usually is, a very efficient process when applied to hydrocarbons, because when burned completely the only products of combustion are carbon dioxide and water. However, if the combustion is incomplete a wide range of additional products such as cracked hydrocarbons, soot and carbon monoxide might be formed. The problem is further complicated if the hydrocarbon that is being burned is halogenated, contains sulfur or is mixed with hydrogen sulfide, because hydrogen chloride and/or sulfur oxides then become products of combustion. In addition, if nitrogen is present, either as air or nitrogenated hydrocarbons, oxides of nitrogen might be formed, depending upon flame temperature and residence time.

Consequently, the definition of efficiency of a burner, as a pollution control device, is difficult. The usual definition of percentage removal of the noxious substance in the feed to the device is inappropriate, because with this definition, a "smoky" flare would achieve the same nearly 100 percent rating, as a "smokeless" one because most of the feed hydrocarbon will have either cracked or burned in the flame. On the other hand, any system that rates efficiency by considering only the total quantity of pollutant in both the feed to and the effluent from the device would be meaningless. For example, the complete combustion of one pound of hydrogen sulfide results in the production of nearly two pounds of sulfur dioxide, or the incomplete combustion of one pound of ethane could result in the production of nearly two pounds of carbon monoxide.

For these reasons, it was proposed that two separate efficiency rating be applied to incineration devices. The first of these is a "Completeness of Combustion Rating" and the other is a "Significance of Emission Reduction Rating", as follows:

1. Completeness of Combustion Rating (CCR)

This rating is based on oxygen rather than on pollutants and is the pounds of oxygen that react with the pollutants in the feed to the device, divided by the theoretical maximum number of pounds that would react: Thus a smokeless flare would receive a 100 percent rating while a smoky one would be rated somewhat less, depending upon how incomplete the combustion.

In utilizing this rating, it is clear that carbon dioxide and water are the products of complete combustion of hydrocarbons. However, some question could occur as to the theoretical completion of combustion when burning materials other than hydrocarbons. It was recommended that the formation of HX be considered complete combustion of halogenated hydrocarbons since the oxidation most typically does not change the valence of the halogen. On the other hand, since some incinerators will be catalytic in nature it was recommended that sulfur trioxide be considered as complete oxidation of sulfur bearing compounds.

Efficiency of Pollution Control Devices

1. Completeness of Combustion Rating (CCR) (continued)

Nitrogen is more complex, because of the equilibria that exist between oxygen, nitrogen, nitric oxide, nitrogen dioxide and the various nitrogen radicals such as nitrile. In fact, many scientists continue to dispute the role of fuel nitrogen versus ambient nitrogen in the production of NO_x. In order to make the CCR a meaningful rating for the incineration of nitrogenous wastes it was recommended that complete combustion be defined as the production of N_2, thus assuming that all NO_x formed comes from the air rather than the fuel, and that no oxygen is consumed by the nitrogen in the waste material. Hence, the CCR becomes a measure of how completely the hydrocarbon content is burned, while any NO_x produced (regardless of its source) will be rated by the SERR as described below.

2. Significance of Emission Reduction Rating (SERR)

This rating is based primarily on the weighting factors that were proposed above. All air pollutants in the feed to the device and all in the effluents from the device are multiplied by the appropriate factor. The total weighted pollutants in and out are then used in the conventional manner of calculating efficiency of pollutant removal, that is pollutants in minus pollutants out, divided by pollutants in, gives the efficiency of removal on a significance of emission basis.

Several examples will serve to illustrate these rating factors. as follows:

Example 1 - One hundred pounds of ethylene per unit time is burned in a flare, in accordance with the following reaction:

$$3C_2H_4 + 7\,O_2 \longrightarrow C + 2\,CO + 3\,CO_2 + 6\,H_2O$$

Thus, 14.2 lbs. of particulate carbon and 66.5 lbs. of carbon monoxide are emitted, and 265 lbs. of oxygen are consumed.

Theoretical complete combustion would consume 342 lbs. of oxygen in accordance with the following reaction:

$$C_2H_4 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O$$

Thus, this device would have a CCR of 265/342 or 77.5%

Assuming that one pound of nitric oxide is formed in the reaction as a result of the air used for combustion (this is about equivalent to 100 ppm), a SERR can also be calculated. It should be noted that the formation of this NO is not considered in calculating a CCR because it came from nitrogen in the air rather than nitrogen in the pollutant being incinerated. The calculation follows:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

Pollutant	Weighting Factor	Pounds in		Pounds out	
		Actual	Weighted	Actual	Weighted
Hydrocarbons	80	100	8000	0	
Particulates	60	0		14.2	852
NO_x	40	0		1	40
SO_x	20	0		0	
CO	1	0		66.5	66.5
Total			8000		958.5

$$SERR = \frac{8000 - 958.5}{8000} \times 100 = 88\%$$

Example 2 - The same as Example 1, except the hydrocarbons are burned to completion. Then,

$$CCR = \frac{342}{342} \times 100 = 100\%$$

and

$$SERR = \frac{8000 - 40}{8000} = 99.5\%$$

Example 3 - One hundred pounds per unit time of methyl chloride is incinerated, in accordance with the following reaction.

$$2\ CH_3Cl + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O + 2\ HCl$$

This is complete combustion, by definition, therefore, the CCR is 100%. However, (assuming no oxides of nitrogen are formed), the SERR is less than 100% because 72.5 lbs. of HCl are formed. Hence, considering HCl as an aerosol or particulate;

$$SERR = \frac{100 \times 80 - 72.5 \times 60}{100 \times 80} \times 100 = 45.5\%$$

The conclusion from this final example, of course, is that it is an excellent combustion device but a very poor pollution control device, unless it is followed by an efficient scrubber for HCl removal.

Example 4 - The stacks of two hydrogen cyanide incinerators, each burning 100 pounds per unit time of HCN are sampled. Neither has any carbon monoxide or particulate in the effluent. However, the first is producing one pound of NO_x and the second is producing ten pounds of NO_x in the same unit time. The assumed reactions are:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

$$4\ HCN + 5\ O_2 \longrightarrow 2\ H_2O + 4\ CO_2 + 2\ N_2$$

$$N_2\ (\text{atmospheric}) + XO_2 \longrightarrow 2\ NO_x$$

Thus, $CCR_1 = 100\%$ and $CCR_2 = 100\%$ both by definition.

However, $SERR_1 = \frac{100 \times 80 - 1 \times 40}{100 \times 80} \times 100 = 99.5\%$

and $SERR_2 = \frac{100 \times 80 - 10 \times 40}{100 \times 80} \times 100 = 95\%$

Obviously, if either of these were "smoky" then both the CCR and the SERR would be lower, as in Example 1.

Other Pollution Control Devices

Most pollution control devices, such as bag filters, electrostatic precipitators and scrubbers are designed to physically remove one or more noxious substances from the stream being vented. Typically, the efficiency of these devices is rated relative only to the substance which they are designed to remove and for this reason could be misleading. For example:

1. The electrostatic precipitator on a power house stack might be 99% efficient relative to particulates, but will remove little or none of the SO_x and NO_x which are usually present.

2. A bag filter on a carbon black plant will remove 99 + % of the particulate but will remove none of the CO and only relatively small amounts of the compounds of sulfur that are present.

3. A water scrubber on a vinyl chloride monomer plant will remove all of the hydrogen chloride but only relatively small amounts of the chlorinated hydrocarbons present.

4. An organic liquid scrubber on an ethylene dichloride plant will remove nearly all of the EDC but will introduce another pollutant into the air due to its own vapor pressure.

For these reasons, it was suggested again that two efficiency ratings be applied. However, in this case, the first is merely a specific efficiency as is typically reported, i.e., "specific to the pollutant (or pollutants) for which it was designed", thus:

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

The second rating proposed is an SERR, defined exactly as in the case of incinerators.

Two examples will illustrate these ratings.

Efficiency of Pollution Control Devices

Other Pollution Control Devices (continued)

Example 1 - Assume that a catalytic cracker regenerator effluent contains 100 pounds of catalyst dust, 200 lbs. of carbon monoxide and 10 pounds of sulfur oxides per unit time. It is passed through a cyclone separator where 95 pounds of catalyst are removed. Therefore,

$$SE = \frac{100 - 5}{100} \times 100 = 95\%$$

$$\text{and } SERR = \frac{(100 \times 60 + 10 \times 20 + 200 \times 1) - (5 \times 60 + 10 \times 20 + 200 \times 1)}{(100 \times 60 + 10 \times 20 + 200 \times 1)} \times 100$$

$$= \frac{6400 - 700}{6400} \times 100 = 89\%$$

Example 2 - Assume that an organic liquid scrubber is used to wash a stream containing 50 pounds of SO_2 per unit time. All but one pound of the SO_2 is removed but two pounds of the hydrocarbon evaporate into the vented stream. Then

$$SE = \frac{50 - 1}{50} \times 100 = 98\%$$

$$\text{and } SERR = \frac{(50 \times 20) - (1 \times 20 + 2 \times 80)}{(50 \times 20)} \times 100$$

$$= \frac{1000 - 180}{1000} \times 100 = 82\%$$